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ECONOMIC GEOLOGY

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THE DATA OF LEAD ISOTOPE GEOLOGY RELATED TO PROBLEMS OF ORE GENESIS [1, 2]

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ABSTRACT

Searching questions about the origins of ore deposits have been asked for many years. Where do ore fluids originate—within the crust, or deeper? Can specific sources of ore metals be identified? When were

[1] Publication authorized by the Director, U. S. Geological Survey.

[2] A summary of this paper was presented orally at the Symposium on The Role of Stable Isotope Research in the Field of Ore Deposits, held by the Society of Economic Geologists, Pittsburgh, Penna., November 1, 1959 (28).

ores deposited? How long did mineralization continue? What was the rate and paragenesis of deposition? Which deposits are cogenetic, and what metallogenetic provinces do they define?

Isotope analyses of lead from rocks and ores provide a new tool for attacking such problems of ore genesis. About two thousand such analyses now available from more than 20 laboratories have been compiled and studied for this purpose. The data now available suggest partial answers to some questions and serve to define other, new problems, not previously recognized. Their greatest import, however, is to illustrate the potential future significance of lead-isotope studies.

Ore-lead, as shown two decades ago, ranges widely in isotopic composition. Recent studies show that traces of lead in ordinary rocks of the earth's crust exhibit apparently similar variations. All these variations are attributable primarily to mixing of old lead with accumulations of new radiogenic lead from decay of radioactive uranium and thorium. Each sample of lead preserves in its isotopic composition a record of its own mixing history: a composite record of the time this lead was in different environments, its past associations with uranium and thorium, and the geochemical processes that moved it from place to place.

Integrated study of all these variables will throw light on many difficult problems of ore genesis when adequate techniques are developed. Progress will be slow, however, until more accurate lead-isotope analyses can be made at lower cost and more objective criteria developed for interpreting measured isotopic compositions in terms of geologic history.

INTRODUCTION

All available lead isotope data have again been evaluated and interpreted for their bearing on problems of ore genesis by staff members of the U. S. Geological Survey. The number of analyses available to us—both published and unpublished data—have multiplied nearly a hundred-fold since 1950 when we last attempted to forecast the importance of lead isotope data for students of ore deposits (17). At that time isotopic analyses had been made of lead from 25 lead minerals, all by Nier (96, 98). Additional analyses began to be published by others in 1952 (35), and by now some 30 laboratories have participated, one way or other, in lead isotope research.

Technical literature reporting lead isotope analyses or interpreting their geologic significance has increased more than tenfold since 1950 when perhaps 500 pages had been written, mostly in discussion of Nier's pioneering analyses. The list of references at the end of this paper includes sources for all the data here reviewed, but only a few of the large number of interpretative papers are listed, for the present paper is an appraisal of available data—not an exhaustive review of the literature. Our summary likewise excludes most of the comparable activity that has been going on in study of lead isotope variations in uranium and thorium minerals for determination of geologic age. Because such radioactive dating results, as applied to ore genesis, tend to have special importance for uranium deposits rather than general significance, they are not included in this paper, even though they are a major phase of lead isotope research.

This worldwide explosion of activity in the last 10 years has been expensive—a rough estimate suggests investment to date on the order of 10 to 25 million dollars. Investment on such a scale shows that many scientists

and administrators are aware of the potentialities of lead isotope techniques to resolve important problems in earth-history that have withstood the assaults of scientists for generations.

Lead isotope data can be expected to shed new light on three major facets of ore genesis: the *sources* from which ore metals were derived, the geologic *processes* that moved them from source to site of deposition, and the *chronology* of mineralizing events. Lead isotope data thus give us chiefly a record of the geologic history of ore-forming materials, unlike isotopic data for lighter elements that commonly give evidence regarding physical-chemical conditions at the deposit during the relatively brief episode of ore formation. Among the light elements, measurable isotopic variations are caused by physical-chemical processes that produce isotopic fractionation as, for example, between a liquid phase and a solid phase that crystallizes from it. In the case of lead, the variations caused by such chemical fractionation are so small that they have not been detected by present measurement techniques. The much larger isotopic variations of lead that we can study, on the other hand, all result, one way or other, from radioactive decay of uranium and thorium. These lead variations, therefore, are products of quite different kinds of geologic history—a sequence of events that permitted the accumulation of new radiogenic lead atoms during long spans of geologic time, or that brought together and mixed isotopically different leads into new products of intermediate isotopic composition.

Our goal here is to evaluate, for economic geologists, the present significance and future potential of lead isotope research, as revealed by the lead isotope data so far available. What we have done is simply to compile and examine the existing data. We have combed the literature for isotope analyses of lead from ore minerals and rocks, tabulated all of these published analyses together with Geological Survey analyses not yet published, recomputed and graphed these data, evaluated their reliability, and studied their variations. We wish this paper could include all available lead isotope analyses compiled in systematic tables and plotted on large-scale graphs so that every reader could experience the satisfaction of exploring these data for himself—but such detailed presentations will have to wait for future publications. Here we can only offer the generalized results of our office study of these data. We merely report what all the data look like when thus compiled, what systematic variations become evident, and what kinds of implications for problems of ore genesis they may have. We find that these data serve to define more clearly some old problems of ore genesis, to reveal many other problems whose existence we did not previously suspect, and to hold much promise for solving these problems in the future. Furthermore, we find a number of ways in which these data can be applied right now as a tool in mineral exploration, even before further fundamental scientific studies are made.

HYPOTHETICAL EVOLUTION OF LEAD

Parent-daughter relationships between uranium, thorium, and lead isotopes, and their relative proportions in earth-crust material, will be illustrated

by the bar diagram Figure 1, in which heights of bars represent atomic proportions of stable isotopes of lead (bottom row) versus radioactive parent isotopes (top row). The diagram shows that Th^{232} disintegrates to form new atoms of Pb^{208}, U^{235} to Pb^{207}, and U^{238} to Pb^{206}, whereas no new atoms of Pb^{204} are thus formed in earth-matter.

The black bars at the bottom of Figure 1 really represent the composition of primeval lead in meteorites, for this is an isotopic analysis ($Pb^{204} = 2.0$, $Pb^{206} = 18.8$, $Pb^{207} = 20.6$, $Pb^{208} = 58.6$ atom percent) by Patterson (101) of lead that he extracted in 1953 from sulfide phase of Cañon Diablo iron meteorite. This troilite contained so little uranium that the isotopic com-

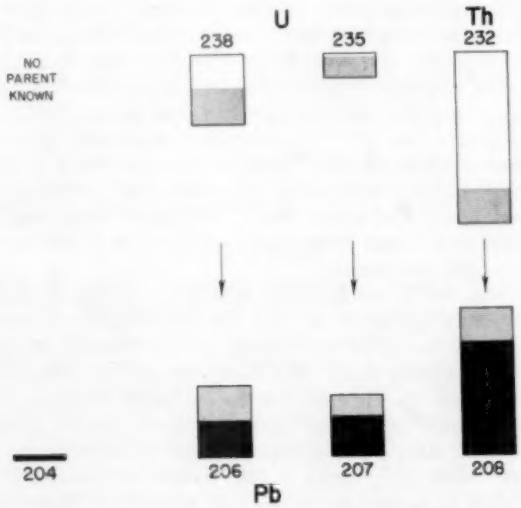


FIG. 1. Isotopic relationships between uranium, thorium, and lead in the earth's crust. Black = primeval lead; gray = uranium and thorium decayed to radiogenic lead during 4.55 billion years; and white = radioactive parent isotopes that still remain.

position of its lead could not have been measurably changed with time (105). This and other data were interpreted (101) to mean that decay of uranium and thorium to stable isotopes of lead has been going on in iron and stony meteorites since about 4.55 billion years ago, when, presumably, a meteorite parent body differentiated into metallic and silicate phases.

One possible basis, then, for guessing what original earth-lead was like is to assume that planet Earth and a hypothetical meteorite parent body were cogenetic. When we try the assumption that lead in earth-matter 4.55 billion years ago was homogeneous and similar in composition to the Cañon Diablo lead, we find that all existing data on composition of earth-leads can be explained conveniently in terms of such a system, as we shall see later.

Consequently, we have adopted this assumption, merely as a convenient frame of reference, throughout our present study of variations among analyzed samples of earth-lead.

Figure 1 represents an earth-model based on this assumption. Heights of bars represent quantitative relationships that have been calculated using reasonable estimates for abundance of uranium, thorium, and lead in the earth's crust. The black bars at the bottom should now be regarded as the *primeval earth-lead* of our model. The gray portions represent decay of radioactive parents (top row) to radiogenic daughters (bottom row) during 4.55 billion years of geologic time. Tops of the lower row should be regarded as an isotopic analysis (1.36, 25.2, 21.3, 52.1 atom percent; calculated) approximating average lead in the earth's crust today—commonly called "modern lead" in lead isotope literature—and the white bars at top of the diagram represent atoms of parents that remain today. According to this model, two thirds of the lead now present in the earth's crust was original, the other third added by gradual accumulation of radiogenic daughters.

This model implies that the whole crust of the earth is like a gigantic hour-glass. Actually, each geologic unit of the crust must be a self-contained lead isotopic clock, for we know that the three radiogenic daughters must accumulate differently in different geologic environments. The important environmental variables are (1) relative abundance of uranium, thorium, and lead in the local environment; (2) geologic time-span during which radiogenic lead atoms accumulate; (3) isotopic composition of starting lead in the environment at the beginning of this time; and at the end of the time-span, (4) the nature of the geologic processes that disturb the environment and extract lead from it. Environmental extremes on a small scale might be illustrated by a pure galena (or feldspar) crystal in which no radiogenic atoms are formed, in contrast with a crystal of uraninite (or zircon) in which the only lead is that produced by decay of the radioelements within it. Between larger portions of the crust environmental and resultant differences will be much smaller, as between granite and gabbro bodies of batholithic proportions. On yet larger scale, the differences that may exist between lead evolved in the crust, the mantle, and the core of the earth are not yet known—except by analogy with meteorites.

Our objective, then, is to measure and study variations thus evolved in isotopic composition of lead, and from them to interpret the geologic history of the sample—that is, to try to reconstruct the previous geologic environments in which our sample of lead has sojourned. In theory, because Pb^{204} is invariant, it is the best yardstick for measuring variations of the other three isotopes. In practice, however, because its abundance is so small (less than 1.65 percent in earth-leads so far tested), Pb^{204} is difficult to measure precisely. Abundances of Pb^{206}, Pb^{207}, and Pb^{208}, on the other hand, tend to be large and measurable with better precision. For this reason, we have reviewed the existing data by examining their variations in atomic abundance of 206, 207, and 208. To do this we recomputed all available analyses to $206 + 207 + 208 = 100$, and plotted them on triangular diagrams, using trilinear coordinates. This mode of presentation is used throughout this paper,

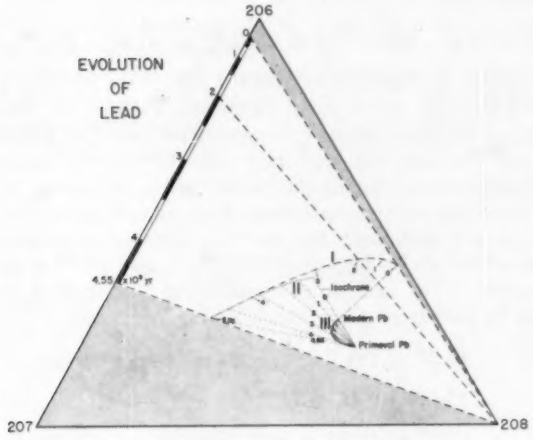
both because of its merits and because it differs from past usage and affords a fresh view of the data. Previous papers on lead isotopes have generally emphasized variations of 204, 206, and 207. Let us be the first to acknowledge that to extract the utmost information from lead data simultaneous variations of all four isotopes must be compared.

Figure 2 is a triangular diagram that represents all possible combinations of the three isotopes, Pb^{206}, Pb^{207}, and Pb^{208}. The white area is intended to represent those compositions of *radiogenic* lead actually generated in earth-material in the course of geologic time—from the lower (dashed) boundary representing all possible compositions being generated 4.55 billion years ago, to the righthand (dashed) boundary representing all compositions of radiogenic lead being generated now. The time scale along the lefthand boundary of the white area represents the clock inherent in all uranium-decay systems and assumes that the present ratio U^{238}/U^{235} is 137.7 (121) in all geologic materials. This scale shows how the Pb^{207}/Pb^{206} ratio of the radiogenic lead being formed has changed gradually throughout geologic time because of the different decay rates of the two parent uranium isotopes. Note that this scale gives the *proportions of Pb^{207} and Pb^{206} formed at each instant—not* the proportions in which they accumulate—in any uranium system such as a crystal of uraninite. Within a more complex system that contains thorium as well as uranium the kind of radiogenic lead being generated 2 billion years ago, for example, would lie somewhere on a line extending from the Pb^{208} apex of the diagram to 2 b.y. on the time scale, at a distance from the apex determined by the Th/U ratio in the system. As a specific example, in a system containing Th/U in a ratio of 4.6 by weight (Curve I), the kind of lead being generated 2 billion years ago is represented by the intersection of the 2 b.y. line with Curve I.

The two gray areas of Figure 2, in principle then, must represent kinds of radiogenic lead that have never been generated on planet Earth, the lower shaded area representing compositions that might have been generated before the earth was born, the area at upper right representing the kinds of radiogenic lead to be formed in all future geologic time.

The composition of lead from Cañon Diablo troilite falls inside the central white area, at the lower tip of Curve III on Figure 2. If this be a valid approximation of the composition of primeval earth-lead, then the white area should represent *all mixtures of lead* that do exist, or have existed, on earth. Our review of available data shows that all analyses of natural lead samples so far published do in fact fall within this area.

The isotopic composition of all lead in the earth's crust must have changed significantly, we know, during the full course of geologic time. We can reconstruct generalized approximations of this evolution of earth-lead by calculating mathematical models, using our analogy with meteorites, in conjunction with reasonable geochemical estimates of abundance of U, Th, and Pb in the crust, and measured physical constants for the radioactive parents. Curve III (Fig. 2) is such a model. For this and similar models in this paper, the following assumptions are made: (1) isotopic composition of



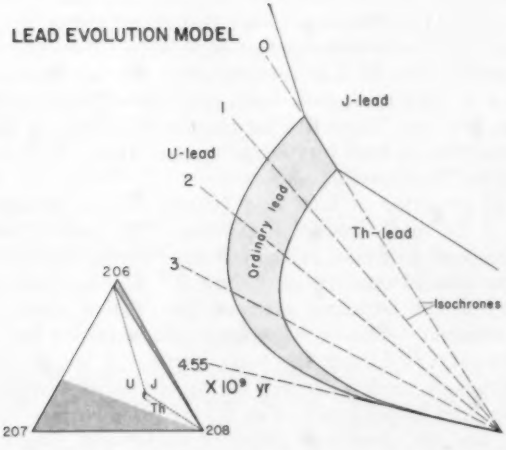


FIG. 2. (Top) Isotopic evolution of lead in a closed system 4.55 billion years old. Curve I. Isotopic variations of radiogenic lead when generated. Curve II. Isotopic evolution of rediogenic lead as it accumulated. Curve III. Isotopic evolution of total lead in system: original (primeval) lead plus radiogenic lead as it accumulated.

FIG. 3. (Bottom) Lead evolution curves representing Pb/U ratios of 6.0 (outer curve) and 7.3, in a system having a Th/U ratio of 4.6 and age of 4.55 $\times 10^9$ yr.

primeval earth-lead was

$$Pb^{204}_{T_0} = 1.0; \quad Pb^{206}_{T_0} = 9.46; \quad Pb^{207}_{T_0} = 10.34; \quad Pb^{208}_{T_0} = 29.44,$$

the same as lead in Cañon Diablo troilite (101); (2) lead has evolved during a period of 4.55×10^9 years, as in meteorites (101); (3) decay constants [3] for uranium and thorium parents have not varied; and (4) relative abundances of U, Th, and Pb (and the important ratio U^{238}/U^{235}) have been changed only by radioactive decay during this period. Any given lead in such a model consists of two components: primeval lead, plus increments of radiogenic lead. And in any such lead the Pb^{204} is entirely of primeval derivation, whereas each of the major isotopes Pb^{206}, Pb^{207}, and Pb^{208} is partly primeval, partly radiogenic. The isotopic composition of lead in such a model at any time (t) can be calculated from the following equations: [4]

$$Pb^{204}_t = 1.0$$

$$Pb^{206}_t = 9.46 + U^{238}_{now}(e^{\lambda 4.55\times 10^9} - e^{\lambda t})$$

$$Pb^{207}_t = 10.34 + U^{235}_{now}(e^{\lambda' 4.55\times 10^9} - e^{\lambda' t})$$

$$Pb^{208}_t = 29.44 + Th^{232}_{now}(e^{\lambda'' 4.55\times 10^9} - e^{\lambda'' t}).$$

Figure 2 illustrates the derivation of one such calculated isotopic evolution model. Curve I is a differential curve that shows the progressive change in composition of *lead being generated at each instant* throughout the period of 4.55 billion years; Curve II is an integral curve that illustrates the *progressive accumulation of such radiogenic* lead; and Curve III is another integral curve that shows how the progressive increments of radiogenic lead gradually modify *the composition of total lead in the system,* from "Primeval Pb" 4.55 billion years ago to "Modern Pb" now.

This model of evolution of *total lead* (Curve III) is enlarged about 10 times in Figure 3 for more detailed inspection. The pair of lead evolution curves here correspond to Curve III and a sister curve, the outer and inner boundaries of the shaded crescent of Figure 2. The two curves represent minor differences in the estimates assumed for relative abundance of lead to thorium and uranium. The Th/U weight-ratio is 4.6 for both curves, but the Pb/U weight-ratio is 6.0 for the outer curve, 7.3 for the inner. Data for these two curves or models, as well as for two other comparable curves used for reference later in this paper (Fig. 9) are assembled in Table I. This table shows also that the abundance ratios of parent and daughter elements assumed in these four hypothetical models are in keeping with estimates derived from chemical analytical data. For the reader's convenience, the assumed chemical weight-ratios are also converted into the atomic ratios one must use to make the model calculations.

[3] Physical constants used throughout this paper are those used by Stieff, Stern, Oshiro, and Senftle (121) in preparing their Tables for the Calculation of Lead Isotope Ages. Their tables can be used to expedite lead evolution calculations according to the equations given here.

[4] Derived from more general equations such as:

$$Pb^{206}_t = Pb^{206}_{T_0} + U^{238}_{now}(e^{\lambda T_0} - e^{\lambda t})$$

A sample of lead extracted from either system (or from *any* comparable system with Th/U = 4.6) and preserved, as galena for example, *3 billion years ago* should have an isotopic composition—then and now—somewhere on the 3 b.y. isochrone.[5] Or any sample of lead extracted *now* from such a system should fall somewhere on the zero isochrone. This is the essence of what has been called "galena dating" (113, and many others).

TABLE 1

LEAD EVOLUTION MODELS

		Solid curves (see Fig. 3)		Dashed curves (see Fig. 9)		Estimates for earth's crust (61,65)
		Outer	Inner	Outer	Inner	
Assumed abundance ratios "now"						
Atomic ratios	Th^{232}/U^{238}	4.75	4.75	4.0	4.0	------
	U^{238}/Pb^{204}	12.0	9.0	9.0	8.0	------
Weight ratios	Th/U	4.6	4.6	3.9	3.9	3 to 5
	Pb/U	6.0	7.3	7.1	7.7	4 to 8
Illustrative geochemical abundances						
(g/ton)	U	3.0	3.0	3.0	3.0	2 to 4
	Th	13.8	13.8	11.7	11.7	7 to 20
	Pb	18.0	21.9	21.3	23.1	16 to 30
Calculated isotopic composition "now"						Primeval lead assumed
Ratios to Pb^{204}	Pb^{206}/Pb^{204}	21.61	18.57	18.57	17.56	9.46
	Pb^{207}/Pb^{204}	17.52	15.72	15.72	15.13	10.34
	Pb^{208}/Pb^{204}	43.62	40.07	38.39	37.40	29.44
Trilinear coordinates	Pb^{206}	26.12	24.97	25.55	25.06	19.21
($Pb^{206} + Pb^{207} + Pb^{208} = 100$)	Pb^{207}	21.17	21.15	21.63	21.58	21.00
	Pb^{208}	52.71	53.88	52.82	53.36	59.79

MEASUREMENT ERRORS

The reliability of any individual published lead isotope analysis must be evaluated if we are to discriminate natural variations from analytical errors. Figure 4 illustrates results obtained by different laboratories on a number of geologic and reference samples. As shown by the diagram, interlaboratory error is commonly two to three times the precision of a single laboratory's measurements. This is well illustrated by the uppermost box of data plotted between the two evolution curves (Fig. 4), showing how two laboratories, despite good reproducibility in repeat analyses, failed to check each other.

[5] "In a diagram representing temporal with other relations, [an *isochrone* is] a line connecting points having the same time co-ordinates" (94). Houtermans (74, 75) used the term in referring to time-lines on graphs of Pb^{207}/Pb^{204} versus Pb^{206}/Pb^{204}, uncomplicated by the effects of decay of Th^{232} to Pb^{208}. Isochrones, as used on our diagrams, involve this one additional variable, but the sense is the same.

Next, the two reference samples GS/4 [6] and NBS 200 [7] shown here represent the most extensively analyzed reference samples known to us. Evaluation of all such comparative data indicates that the confidence we may place in a single published analysis, in comparing data from many laboratories, is ± 0.5 percent of the reported Pb^{206}, Pb^{207}, and Pb^{208} abundances. The magnitude of this error is indicated by the ellipse in the upper righthand corner of Figure 4. For Pb^{204} the corresponding uncertainty of reported abundances is perhaps five times greater, covering a substantial fraction of its abundance range. This is one of the reasons for not including Pb^{204} data in this review.

Translated into terms of geologic history, this analytical uncertainty (Fig. 4) in comparing a single published analysis with data from other laboratories

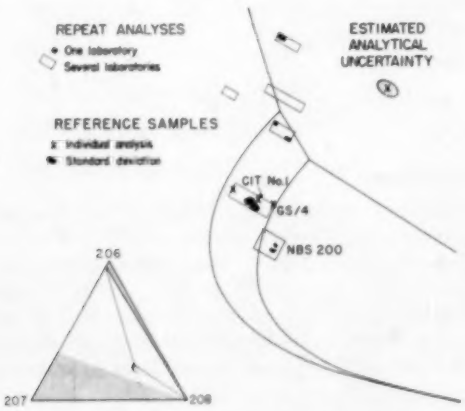


FIG. 4. Measurement errors in published lead isotope data. Black rectangles represent several analyses of the same sample by one laboratory; open rectangles represent analyses of the same sample by different laboratories. Black ellipses represent the mean value and standard deviation of many analyses of a reference sample by one laboratory. The comparative analytical uncertainty of any single analysis is depicted by the gray ellipse.

is ± 150 million years. This 300-million-year uncertainty is equivalent, more or less, to the span of geologic time from mid-Paleozoic to the present, and puts a severe limitation on geologic interpretations based on existing data from many laboratories. For analytical data from a single laboratory, however, the uncertainty is generally much smaller because of better internal precision. Also we anticipate that effective steps will gradually eliminate discrepancies in results from different laboratories.

The most precise results by any laboratory that have come to our attention

[6] GS/4 is spectrographically pure lead metal distributed to various laboratories some years ago by L. R. Stieff, U. S. Geological Survey.

[7] NBS 200 is galena from the cryolite deposit at Ivigtut, Greenland, available in limited quantity from Dr. Fred L. Mohler, National Bureau of Standards, Washington 25, D. C. (92).

are shown by the small solid black rectangle[8] just above the GS/4 data. The deviation here is about a part per thousand, and illustrates the good precision that can be obtained under optimum conditions with present-day instrumentation (32).

An improvement of perhaps two or three times in equivalence of data could result from judicious use of a common reference sample for calibrating results from all laboratories. Such a reference sample (NBS 200) was established several years ago (91) for distribution in limited quantities for this purpose. Until absolute standardization becomes possible, keying all analytical data to this reference lead would be of great value, for no individual laboratory can afford the expense of analyzing all the critical samples needed for interpreting its data. An even more fundamental improvement will be made, moreover, when it becomes possible to check the accuracy of measured values against "absolute" standards prepared from purified isotopes.

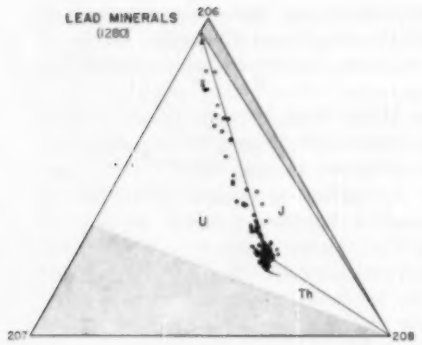
The need for precision and accuracy in isotopic measurement of ore-lead is greater than is generally recognized. The isotopic variations we wish to interpret are much subtler, for example, than those measured for radioactive dating studies. The increment of radiogenic lead generated during a given span of geologic time may be clearly recognizable in a radioactive mineral but inconspicuous in ordinary lead where the new atoms are greatly outnumbered by pre-existing lead atoms. This contrast is illustrated in Figure 2 by the small change in isotopic composition from primeval lead to modern lead (Curve III), as compared with the far larger variations possible among radiogenic leads, represented by the entire white area of the diagram.

ISOTOPIC COMPOSITION OF LEAD IN ORES AND ROCKS

Lead isotope data are presented throughout this report in terms of $Pb^{206} + Pb^{207} + Pb^{208} = 100$, on trilinear coordinate graphs. To illustrate major variations the full triangular diagram, as in Figure 2, will be used. For greater detail an enlargement of the central portion of the triangle will be used, showing our crescentic or horn-shaped evolution model, as in Figure 3, for scale and orientation. To facilitate empirical description we divide the whole lead field, as shown in Figure 3, into four sectors by joins from the zero isochrone of the evolution model toward the two zero apices of the white area—that is, to pure thorium-lead and to pure uranium-lead being formed today. Analyses that plot in these sectors will be described as (1) *ordinary lead* in the crescentic area between the two evolution curves, (2) *U-lead* in the sector extending from the ordinary-lead field toward pure uranium-leads of the past, (3) *Th-lead* in the opposite sector toward the Pb^{208}-apex, and (4) *J-lead* in the triangular area beyond the zero isochrone of our evolution model in the direction of present and future radiogenic leads.

All available data from nonradioactive ore minerals, then, have been plotted on the triangular graph (Fig. 5). After some effort to eliminate or minimize duplicate analyses, such data total 1280 isotopic analyses of lead—

[8] Results by staff at California Institute of Technology on their own reference sample CIT Shelf Standard No. 1.



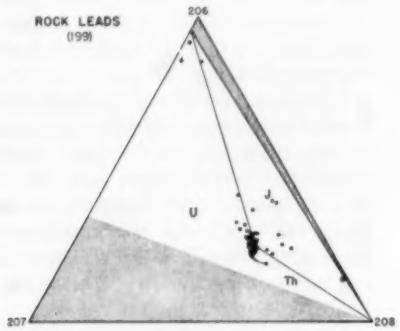
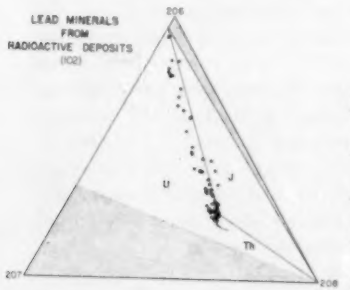


FIG. 5. (Left) Isotopic composition of lead from 1280 ore minerals—plotted in terms of $Pb^{206} + Pb^{207} + Pb^{208} = 100$.

FIG. 6. (Right) Isotopic composition of 199 samples of rock-lead.

mostly from galena, plus a few from other lead minerals like bournonite, from other ore minerals like pyrite, or from bulk ore samples. Similarly, Figure 6 presents the available analyses that represent various kinds of lead contained in small amounts in rocks of the earth's crust. These 199 analyses include lead extracted in the laboratory from rocks such as granite, basalt, and limestone, from marine sediments such as deep-sea manganese nodules, from rock-forming minerals such as feldspar, but exclude most analyses of lead from highly radioactive rock-forming minerals such as zircon. The data do include, in addition, some samples of lead extracted recently by natural processes from rock-materials and concentrated in available form, such as volcanic sublimates.

Variations in composition in these two populations of data—ore-leads (Fig. 5) and rock-leads (Fig. 6)—are fairly similar. The distribution scores



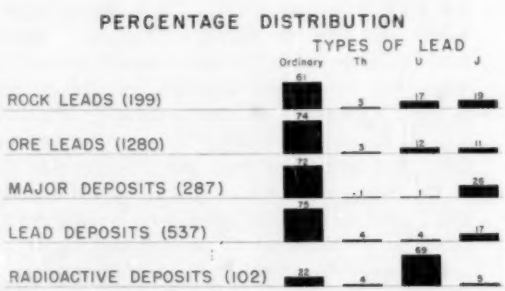


FIG. 7. (Left) Isotopic composition of lead from galena or other nonradioactive minerals from uranium or thorium deposits or districts.

FIG. 8. (Right) Some statistical variations in isotopic composition of lead from different environments.

tallied in Figure 8 show this similarity and bring out several other striking relationships. Nearly three-fourths of all these ore-leads and nearly two-thirds of these rock-leads fall in the small ordinary-lead field between the two curves of our hypothetical evolution model. On the other hand, out of 102 samples of lead from galena and other nonradioactive ore minerals from uranium (or thorium) deposits and districts, less than one-quarter are ordinary lead and more than two-thirds are U-type lead. These samples from radioactive deposits, plotted alone on Figure 7, account for about half of the U-type analyses among the 1280 ore-leads (Fig. 5).

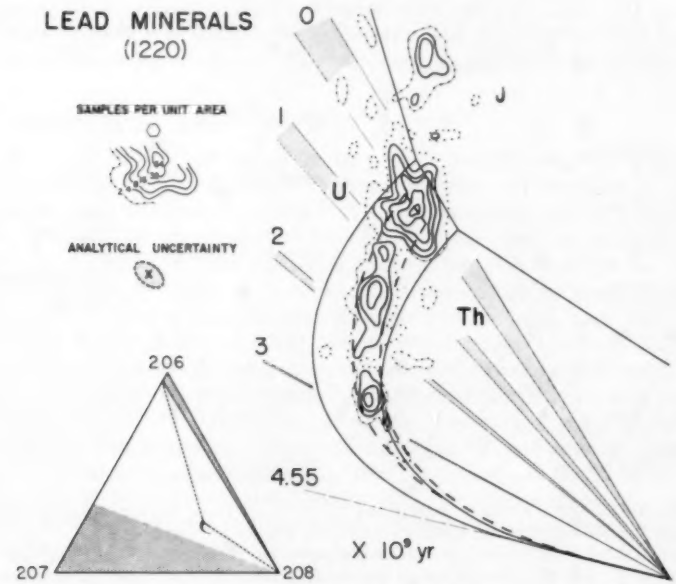


FIG. 9. Isotopic variations of ore-lead from 1220 ore minerals. Contours show distribution of data in excess of a single sample per unit area.

SOME ISOTOPIC VARIATIONS OF ORE-LEAD

Now let's examine some isotopic variations of ore-lead in more detail. At the enlarged scale, 95 percent of the 1,280 ore-leads plot within the limits of Figure 9. The frequency distribution of these 1220 points is shown by contouring the number of samples that fall within each unit-area like the hexagon shown in the explanation. The outermost contour encloses all unit areas that contain more than a single point. A maximum concentration of points enclosed within the highest contour is 69 points per unit area. This maximum represents a concentration of points about 5,000 times greater than homogeneous distribution.

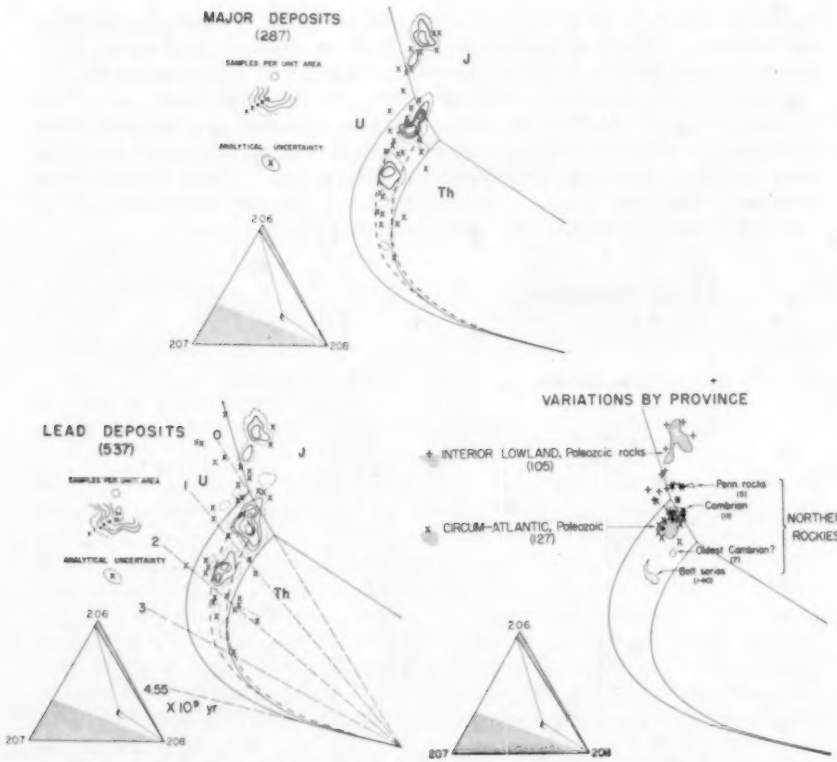


FIG. 10. (Top) Isotopic variations of ore-lead from major mineral deposits. A single sample outside the lowest contour is shown by symbol X.

FIG. 11. (Left) Isotopic variations of ore-lead from deposits of lead ore.

FIG. 12. (Right) Variations of ore-lead in several provinces. Distribution of data delineated by shading, except for scattered single samples shown as + (Interior Lowland Province), × (circum-Atlantic regions), and * (intervening Folded Appalachian Province).

Categories of Ore Deposits

These data can be sorted out in various ways to look for isotopic variations that correlate with important geologic factors. Information on the geologic occurrence of most samples reported in the literature is so meager that only a few elementary tests of this kind can be made on data so far published. Figure 10 is an attempt to sort out and synthesize data from only the big mineral deposits. Lead mines or districts were included if production plus reserves exceed 100,000 tons of lead metal. We tried to set comparable standards for deposits of other commodities. A majority of the data represent major producers of lead, but about a fifth of them are from

deposits in which lead is not a major constituent. These include major deposits of iron, copper, manganese, tungsten, tin, aluminum, zinc, nickel, gold, and rare earths. On this graph there is much less scatter of points—every individual analysis outside the lowest contour is represented by an X. Excepting area J, data from major sulfide deposits fall in a narrow band whose width scarcely exceeds the analytical uncertainty. Thus these data are even more consistent with a hypothetical model, possibly because a large ore deposit is simply a better geochemical sample.

Figure 11, similarly, should give a reasonable picture of what lead in lead-ore deposits is like. Data from major and minor lead mines and from lead prospects have been included, whereas data from deposits that produce only other commodities have been excluded. The distribution pattern here is fairly similar to Figure 10, but with more erratic scatter of individual analyses.

Variations by Province

Data now available do not seem to provide simple rules for predicting the kind of lead to expect within a given province, nor whether it will be uniform or variable in composition. We have compiled data for three examples, shown in Figures 12 and 13. Lead in ore deposits, enclosed predominantly in rocks of Paleozoic age, around the perimeter of the North Atlantic from North Carolina to Newfoundland to Spain is almost invariant in composition. All of the 127 analyses plot near the zero isochrone of our hypothetical model within a small area scarcely larger than the analytical uncertainty. In the neighboring Interior Lowland Province of North America, on the other hand, ore deposits in Paleozoic sedimentary rocks contain quite different lead (105 samples), markedly J-type, and more variable in composition. The geographic limits of this kind of lead are not presently known. To the east, two samples (7) from ore deposits in the Folded Appalachians—at Mascot, Tenn., and Friedensville, Pa.—have reported compositions intermediate between the two types. These two samples are shown on Figure 12 by special symbols (X superposed on +). A third exotic sample, galena from a lead prospect in Mississippian limestone, Uinta Range near Vernal, Utah (22), is plotted on Figure 12 (symbol + above the "i" in "province") as an extreme example of such lead found in Paleozoic rocks on to westward from the Interior Lowland. In the Northern Rocky Mountain province even greater isotopic variation has been reported than in the Interior Lowland. There, the younger the sedimentary host rock, the more radiogenic the lead in the ore deposit, a generalization that we expect to become less tidy as additional data accumulate. The most primitive leads so far analyzed from the Northern Rockies are a large number of samples (lowermost cluster, Fig. 12) from Montana, from Coeur d'Alene, Idaho, and from Sullivan and other ore deposits in British Columbia, all in sedimentary rocks of Precambrian age; next, seven samples from the Bluebell mine, B. C. (120), in rocks of the Windermere Series, probably lowest Cambrian or uppermost Precambrian; next, on our zero isochrone, 11 samples from deposits in Cambrian limestones at Metaline, Wash., and in nearby British

Columbia; finally, five samples of J-type lead from the Minnie Moore mine, Idaho (7), in marine sediments chiefly of Pennsylvanian age. In summary these data indicate that lead evolution has had a different history in different provinces. There is reason to expect that, as more data became available, generalized evolution models such as those used in this paper will be supplemented by more detailed models describing lead variations in specific geologic provinces.

Variations by District

Within single districts, likewise, comparable instances are known of both remarkable uniformity and unpredictable variation. Noteworthy variations have been found in single mines, even within a single crystal of galena (18). Isotopic analyses of samples from five successive growth layers of a large crystal of galena from the Tri-State district (130) show progressive increase in radiogenic isotopes from an inner layer (butt of black arrow, Fig. 14) to an outer layer (tip of arrow).

Figure 14 also shows variations in ore-lead in the northwest Adirondacks, N. Y. (15), in the Broken Hill district, N. S. W. (112), and in Yavapai Co., Ariz., and the Park Range, Colo. (130). In each of these four districts, in regionally metamorphosed Precambrian terranes, an "older" type of lead has been found in massive sulfide deposits, possibly synkinematic, and a "younger" type in postkinematic fissure veins, which may or may not be of much younger geologic age. On this latter point there is evidence at one of the localities, for one of the Rossie fissure veins has been reported (15) to cut a sedimentary cover of Cambrian age. Possibly analogous with these four examples is the more extreme variation found in the Sudbury district, Ontario. Much has been written about the two different types of lead at Sudbury, which we can illuminate with evidence from three galenas collected there in 1953 from different geologic settings by Cannon and L. T. Silver (unpublished data). Two of these galenas are from quite different types of Precambrian deposits of minable ores: one an integral constituent of copper-nickel ore at the base of the Sudbury norite (Frood mine), the second from one of the pyritic copper-lead-zinc deposits in roof rocks of the norite in the interior of the Sudbury basin (Vermilion mine). These two ore-leads are identical in composition and plot just above the 2 b.y. isochrone. The third sample is quite different, J-lead, collected from thin films of quartz-galena on joints that cut copper-nickel ore (Frood open-cut). We have no reason to assume that this trace occurrence of galena had any direct genetic relationship to any ore metallization in the Sudbury district.

Referring again to Broken Hill, the lead of this district is noteworthy for uniformity as well as for variation. As reported by Russell and others (112), analyses of six samples of lead from the Broken Hill main lode are virtually identical—within limits of error—and plot somewhat above the 2 billion year isochrone. Eleven samples from smaller outlying deposits that are similar ore lenses of "Broken Hill type" (78), conformable with the steeply folded gneisses, are indistinguishable from the main lode samples. But eight samples from other outlying deposits, lower temperature vein de-

posits of "Thackaringa type" (78), plot above the 1 billion year isochrone and are much more variable in composition.

SOME GENETIC IMPLICATIONS

Lead isotope research has not yet progressed to the point of telling us how ore deposits were formed. But the data presented here in generalized form show the sorts of interpretations concerning fundamental problems of ore genesis we should expect from future lead isotope studies. What can lead isotopes reveal then about the geologic sources of ore-lead, about the geologic or geochemical processes that mobilize it and move it from source to sink, and about the times the ore-lead spent in earlier environments and the timing of its final deposition?

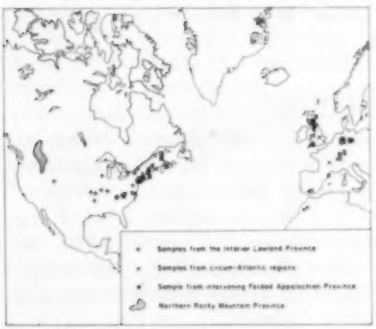
Orderly Evolution of Ore-lead

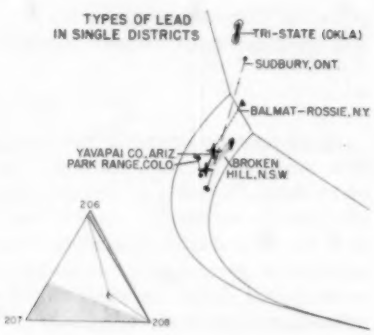
A majority of analyzed ore-leads coincide with the hypothetical model of Figure 3, defined by a pair of calculated evolution curves. About 83 percent of ore-leads, excluding the minor percentage of leads in area J, fall within this model (Figs. 8 and 9). For present purposes we term these *ordinary leads*. The remaining 17 percent fall outside the ordinary-lead field, to right or left, in areas Th or U. For lead-ore deposits about 90 percent of samples are ordinary leads (versus 10 percent in areas Th and U), and for major mineral deposits an even more remarkable 97 percent.

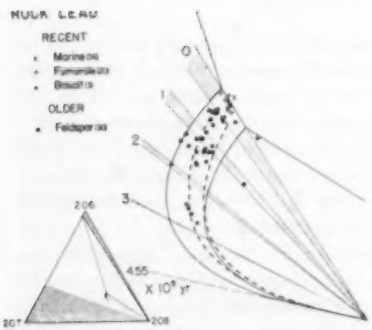
Other evolution curves can be calculated to fit the data, especially for major deposits, even more closely. The two dashed curves of Figure 10 are such a pair of calculated curves for a hypothetical system with Th/U ratio of 3.9 and Pb/U ratios of 7.1 and 7.7 (Table 1). These calculated curves enclose a narrow crescent whose width approximates the analytical uncertainty, as shown by the gray ellipse (Fig. 10). Data from 73 percent of all localities which have been sampled plot within this narrow crescent. This striking coincidence between experimental data and calculated model strongly suggests that a high proportion of ore-leads are indeed the offspring of some simple evolutionary system.

Now, let's review various kinds of geologic environments that may give rise to leads that fit this model. One simple concept is that some segment of earth-structure, distributed generally beneath the continents, remained virtually a closed system, unaltered by geochemical change throughout geologic time except for giving birth, once in a while, to minor quantities of ore metals. Hypotheses that ore metals are derived from a primordial layer or other source in the depths of the earth, such as those suggested by Gregory (67), Holmes (70), Brown (14), and others, might be in accord with such a concept.

Some alternative hypotheses may deserve equal consideration. One is that igneous and metamorphic processes may not be very effective in changing the relative proportions of uranium, thorium, and lead. If so, these three chemical elements should have more or less the same abundance ratios in crystalline rocks regardless of time or mode of origin, and the evolution of







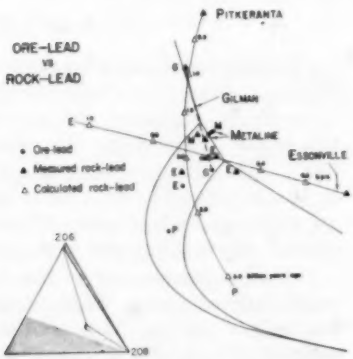


FIG. 13. (Top left) Geographic distribution of samples represented on Figure 12.

FIG. 14. (Top right) Some isotopic variations of ore-leads (galenas) within single mining districts. *Tri-State:* single crystal: open circles = successive growth zones; heavy black arrow = generalized trend from inner to outer zones. *Sudbury:* upper dot = joint coatings in Frood open-cut; lower dots = Frood Cu-Ni, and Vermilion Cu-Pb-Zn ore. *Balmat-Rossie:* upper triangle = Rossie vein; lower triangles = Balmat and Edwards ore bodies. *Broken Hill:* upper black area = Thackaringa-type veins; smaller, lower black area = main lode and similar deposits. *Yavapai County:* upper + = Hillside Pb-Zn vein; lower + = Iron King Cu-Pb-Zn deposit. *Park Range:* upper dots = Three Forks (Wyo.) and Elkhorn Pb fissure veins; lower dots = Greenville and Slavonia Cu-Pb-Zn deposits.

FIG. 15. (Bottom left) Isotopic variations among 59 samples of rock-lead of Recent geologic age compared with 30 older rock-leads of different ages.

FIG. 16. (Bottom right) Comparison of ore-leads with rock-leads to test for genetic relationships.

lead would be similar in many different geologic environments. This concept must be weighed seriously, for there is evidence of some tendency toward stability of geochemical abundance ratios of these three elements. In sedimentary rocks, however, uranium-thorium-lead ratios appear to vary more widely. A third hypothesis thus might be that various cyclical processes

continuously tend first to change, then to restore, average proportions for these elements.

The crude data so far available permit entertaining any one of these alternative hypotheses. Ordinary ore-leads might have evolved in a basaltic subcrustal layer now containing, for example, 1 g/ton U, 4.1 g/ton Th, and 7.3 g/ton Pb; or equally well in some sialic environment now containing three or four times as much of each of these, say 3.5 g/ton U, 14.4 g/ton Th, and 25.6 g/ton Pb.[9]

Lead isotope data have suggested these hypotheses, and better lead isotope studies are the best tool we know for investigating them further. The possibility is suggested above that lead might have evolved similarly in a variety of geologic materials or environments. If this should prove true, then the capacity of lead isotope variations to date events of geologic history will be enhanced but their ability to reveal the nature and sites of these events will be reduced. In any case, we should expect to learn certain things from this orderly evolution of lead, and other quite different things from so-called "anomalous leads" that appear to be exceptions to orderly evolution.

Sources of Ore-lead

Future lead isotope studies designed to resolve our present uncertainty will probably reveal whether ordinary ore-leads come from a nearly closed system deep within the earth, or elsewhere in earth-structure, or whether they come from various heterogeneous geologic sources so interrelated as to yield a family of orderly evolution products. Likewise, more refined lead isotope research will doubtless determine what different kinds of sources have produced the less abundant "exceptional" leads of Th-, U-, and J-types. Even now, we can be sure that these four types of lead have had different geologic histories.

One of the most fundamental problems about the provenance of ore-lead can be evaluated with the help of lead isotope data. This is the question whether lead in ore deposits is like or unlike the traces of lead intrinsic in different species of rocks. Figures 6 and 5 have shown us already that isotopic variations among rock-leads resemble in a general way those in ore-leads, and Figure 8 shows that rock-leads, almost to the same extent as ore-leads, are predominantly ordinary leads.

Some rock-lead data are plotted in more detail on our evolution models (Fig. 15). The plotted symbols represent nearly 60 samples of "modern" rock-lead extracted from basaltic lavas, fumarolic deposits, and marine sediments—all from rocks that, figuratively at least, are just being formed today. These then, are rock-leads of zero age, and all of them plot in the zero isochrone region of our two models. Also plotted are the available data on lead extracted from feldspars of rocks of various ages. These feldspar data,

[9] A single curve constructed to approximate the ore-lead data of figure 9 as closely as possible would correspond to an evolutionary system with Pb/U ratio of 7.3 and Th/U ratio of 4.1. In the statement above, these ratios have been translated into terms of abundances that closely approximate chemical analytical data so far determined for basaltic and granitic rocks (56, 69, 115, 119, 132).

although meager, are important because a large fraction of the lead of the earth's crust is locked in feldspars. Also, because most feldspars are poor in uranium and thorium, they preserve with little change a sample of the lead that was present when the rock crystallized. About 90 percent of these feldspar-leads plot within the area of the model (solid curves), and, as with lead from major mineral deposits, there is amazing coincidence of these leads with the revised evolution model (dashed curves). In addition, there is a tendency for model ages of these feldspar-leads to agree with age of host rock as deduced from independent evidence. Implicit in all of these observations is a strong possibility that common rocks of the earth's crust may have been the source of metals in many ore deposits.

One of the most hopeful possibilities for exploring the source of ore metals with lead isotope techniques is to examine lead in associated rocks and ore deposits, blood-typing them in effect, to test whether the rock could have been the parent of the ore. In contrast with applications discussed heretofore, these are detailed tests of specific case histories. To date, practically no such studies have been made, but some imperfect examples, assembled in Figure 16, can be described briefly just to illustrate this approach. In the Metaline district, Wash., lead in feldspar of the Kaniksu batholith should be studied to test whether lead in the Kaniksu magma when it crystallized was like or unlike the lead in ore deposits in adjacent Metaline limestone. This feldspar-lead has not yet been analyzed, but the two analyses plotted here as rock-lead are from a trace occurrence of galena in altered monzonite far within the batholith (130), apparently deuteric mineralization. The data plotted on Figure 16 suggest that the batholith could have been the source of Metaline ore-lead.

Also shown on Figure 16 are evolution curves for total lead in two granites, calculated as closed systems backward in time from measurements of abundance of U, Th, and Pb and isotopic composition of total lead now in rock specimens. The calculated path of change for lead in "Essonville granite" (126) is consistent with the kinds of lead analyzed from perthite and plagioclase from the same specimen, but not consistent with lead in perthite of a nearby pegmatite, nor with lead in galena of the nearest ore deposit tested (126). Data for "Pitkeranta granite" (142) and for galena from skarn at its contact (142) likewise are not perfectly consistent, but the analytical uncertainties do permit a possibility that granite and galena might have been cogenetic some 2½ billion years ago.

Finally, trace-lead in a sample of Leadville limestone is so unlike lead in a sample of galena from ore that replaces this limestone (54) that Gilman ore-lead could scarcely be a concentration of this rock-lead.

Not one of these is completely satisfactory as an illustration, but future experiments, if well planned and executed, will certainly provide diagnostic evidence to show whether a specific ore-lead could have had its source in a specific rock or magma.

Another kind of evidence concerning sources of ore-lead comes from data on provincial variations. The data generalized in Figures 12 and 13 have various implications as to source. Ore-lead in deposits around the perimeter

of the North Atlantic is remarkably uniform, and this may be part of an even more widespread phenomenon, for many samples from around the perimeter of the Pacific also have this composition. If this proves to be a real phenomenon, perhaps ores around present continental margins have been derived from some common source. Secondly, J-leads seem to be a regional phenomenon, for they have been found almost exclusively in the interior of North America. These too evidently have in common some unique factor in their geologic history. A common source? Or some special geologic process?

Chronology of Mineralization

For each ore-lead with composition in the ordinary-lead field a "model age" can be calculated—or obtained by graphic solution (Fig. 3)—from isotopic composition alone. "Model age" merely means that if a sample of lead evolved inside a closed system having specified characteristics, then it must have been extracted from such system the calculated number of years ago. Actually, most ordinary ore-leads do have model ages that seem to be geologically reasonable.

J-leads, on the other hand, lie beyond the zero isochrone of our specified evolution model—that is, they have "future" model ages—and are probably not products of orderly evolution in such a system. Some U- and Th-leads similarly lie beyond the zero isochrone; others lie within the isochrones. Some of these latter U- and Th-leads could be products of some such system; others surely are not. Hence "galena dating" might properly be applied to some of these, not to others. We still need to learn how to recognize the samples that can be appropriately dated by model age. And we need to learn precisely what model shall be applied to which samples. Then we shall have acquired a powerful tool.

The remarkable coincidence of ordinary leads with calculated evolution curves in Figure 9 almost surely implies that these samples are amenable to some form of model dating. Equally remarkable is the concentration of hundreds of analyses within the dashed model in three or four distinct clusters or maxima clearly defined by the contouring. Their centers are located successively at about the zero isochrone (largest cluster), 1 (smallest), 1½, and 3-minus billion year isochrones. These maxima might be explained as products of inadequate sampling. More likely they reflect major epochs of mineralization. In this regard it is interesting that modern radioactive dating studies (e.g. 125) tend to show a comparable periodicity of *rock ages.*

A review of the geologic occurrence of the samples that populate these clusters suggests some kind of relationship between composition of lead in ore deposits and age of enclosing country rocks. The "oldest" maximum, near 3 b.y. isochrone, represents deposits in Precambrian rocks of which some are known to be extremely old; the next, near 1.5 b.y., includes deposits in Precambrian rocks of which none are known to be extremely old; and the largest, near zero b.y., includes deposits in younger rocks, of Paleozoic, Mesozoic, or Tertiary age. This apparent correlation of model age with age of host rock is perhaps expectable. In environments of crystalline rocks, in

particular, magmatic ore deposits should be of the same age as associated parental igneous rocks, and the age of synkinematic deposits will, *a priori*, correspond to the date of metamorphism of enclosing metamorphic rocks.

The time required to form a given ore deposit is a problem of ore genesis that has been largely ignored for want of suitable measuring devices. If ores are formed rapidly, in terms of geologic time, a suitable chronometer may be hard to find. However, if some deposits form slowly during long periods of geologic time, then evidence of slow growth might be recorded by progressive isotopic variations of the lead deposited. The variations we have found within a single crystal of galena (Fig. 14) might be interpreted as such a phenomenon. This is a clue that we are impatient to follow up to test whether the isotopic variations can be resolved in terms of rate and duration of crystal growth and ore formation. But these are variations so close to the present limits of analytical error that further study cannot profitably be made until analyses of better accuracy and precision can be obtained.

Processes of Mineralization

The deposition of any ore is necessarily the culmination of a long chain of geologic events. We can imagine a succession of geologic processes, involving first of all the creation of some geologic body that could serve as a source of ore metals. Other processes might later affect this source, selectively extracting ore metals, transporting them from source to site of deposition, and ultimately depositing metals as ore. Lead isotope studies may give information about many such processes, but particularly those at the source, the ones most likely to leave their imprint on the isotopic composition of ore-lead. Ordinary leads in a majority of ore deposits have systematic isotopic variations that seem to brand them as products of some common process, whereas the quite different compositions of U-, J-, and Th-leads must have originated by more or less different processes. Future studies should resolve our present uncertainty whether ordinary leads evolved by long gestation within some worldwide closed system or were generated in various local geologic environments. It seems reasonable to expect, moreover, that we shall learn what gave rise to the periodicity we have observed in ordinary lead data. Meanwhile, several generalizations about the populations of ordinary leads contoured on Figures 9, 10, and 11 suggest a few clues.

Ore-leads from major deposits (Fig. 10) fit a simple model more closely than do all ore-leads (Fig. 9). Did ore-forming processes tend to deviate more widely from some norm when forming small deposits? Or did some process work better when handling large tonnages of materials? Or were large tonnages of metal less readily contaminated by extraneous lead?

The "oldest" maximum concentration of ordinary leads, near the 3 b.y. isochrone on Figure 9, is populated chiefly by minor gold deposits and a few minor lead deposits. Evidently a few major gold mines are represented, but no major lead mines are known to have this composition. Did ore-forming processes in early geologic time lack some prerequisite for concentrating vast tonnages of lead, or other metals, into ore deposits? Or were sources of

ore-metals not so rich as those in later geologic time? Or will more data change this picture? These are representative of the many problems that have been discovered and barely defined by lead isotope data—but not yet investigated.

Leads with compositions outside the ordinary-lead field—called "exceptional leads" in this paper—constitute a respectable minority making up 26 percent of all analyzed ore-leads. These exceptional ore-leads may have even more to tell us about ore-forming processes than the ordinary leads. Exceptional leads include the three categories (Fig. 3): Th-leads, J-leads, and U-leads. U-leads and J-leads each make up more than 10 percent of ore-lead analyses, but Th-lead data are only a few percent of the total.

Th-leads are more enriched in Pb^{208} than ordinary leads. Not much is known about them, for relatively few occurrences have so far been found. More than half of the reported analyses of Th-lead occur in a cluster at the 2 b.y. isochrone of our model (e.g. Fig. 11). These represent galenas from three localities—the Ivigtut cryolite deposit, Greenland; the Outokumpu copper deposit, Finland; and pegmatites in Karelia, USSR—two of which are major mineral deposits. About processes that have given rise to Th-leads we can say little except that, if any Th-leads were produced by orderly evolution, then their sources must have been abnormally rich in thorium, or in original lead, or in both.

U-leads are those more enriched than ordinary leads in radiogenic Pb^{206} and Pb^{207}. We wish to discuss primarily U-leads from nonradioactive minerals such as galena or pyrite—excluding radiogenic leads from uranium minerals such as uraninite. Such U-leads may originate either by orderly evolution during a long span of geologic time or by "instantaneous" mixing of two different leads. About U-leads produced by mixing we have abundant evidence from uranium-mining districts; about possible examples produced by evolution we know little. If there are segments of the earth's crust that contain more than a proportionate share of the earth's uranium, we may expect such a province to be characterized by an evolution series of U-leads of various ages plotting along a curve parallel to the U-side of the ordinary-lead field. Any earth-segment that has a Pb/U ratio less than 6 or a Th/U ratio less than 4.5 might be expected to give rise to some such series of U-leads. We know of no other criterion that would better identify a real uranium province.

A fairly detailed digest of lead isotope data from radioactive ore deposits by Cannon, Stieff, and Stern was published in 1958 (29). Here we can only recapitulate a few highlights with statistics improved somewhat by broader coverage of data. Out of 102 leads known to represent samples from uranium (or thorium) districts 69 percent are U-leads, as compared with 7 percent U-leads among all other samples. Suites of data from individual uranium districts tend to form rectilinear patterns indicating that such leads are mixtures of two components: an ordinary lead, and a radiogenic lead from uranium decay (Fig. 17a, b, c, d). The Pb^{207}/Pb^{206} ratio of the radiogenic component in these leads tends to be characteristic and nearly constant for each uranium district. The ratio for different districts correlates in a

fashion with ages of the ores and their country rocks, for the ratio tends to be high (i.e. "old") in old deposits in old environments, and *vice versa*. Further, the ratio tends to be higher in galena-lead than in uraninite-lead from the same deposit by some 3 to 20 percent (compare the two ratios at upper left on Fig 17a, b, d). Finally, in several districts where uranium ore contains some thorium, galena-lead also contains variable amounts of radiogenic Pb^{208} so that a group of analyses deviates from linear geometry (Fig. 17e, f). Two galenas from Blind River, Ont., (138) evidently contain enough radiogenic Pb^{208} to put them into area J (Fig. 17e).

The geologic types of uranium ores with which suites of U-leads have been found associated so far include carnotite-uraninite-coffinite deposits of sandstone-type (Colorado Plateau); veins of disseminated uraninite (Dripping Spring quartzite, Ariz.); pitchblende veins (Goldfields, Sask.); a uraninite vein in a lead-zinc-silver district (Sunshine mine, Coeur d'Alene district, Idaho); and gold-uranium-thorium-bearing Precambrian conglomerates (Blind River, Ont.; Witwatersrand, So. Afr.)—all illustrated in Figure 17. In one major uranium district (Katanga, Belg. Congo) only slight evidence of U-lead has been found; in one other, none (Great Bear Lake, N. W. T.). More exhaustive sampling of these districts may yet discover the presence of U-leads.

Existing evidence seems ample to demonstrate that these U-leads from radioactive deposits are products of a mixing process, but more detailed interpretations of the nature and timing of this process are still uncertain. Did the mixing take place at the source of the uranium, or at the ore site just prior to deposition, or by chemical redistribution of lead within the deposit long after its formation? As soon as we have evidence that answers these questions, we shall be much better informed about the origins and dating of uranium ore deposits.

J-leads are exceptional leads defined by their geometric position beyond the zero isochrone of our model diagram as shown in Figure 3. These leads are so enriched in radiogenic isotopes that when related to our ordinary evolution model, their isotopic compositions would imply impossible "future model ages". In this sense, we regard them as the mystery-thriller of lead isotope geology. One of their characteristics is isotopic variation within local districts; and deserving of special notice is evidence at two separate localities that isotopic composition of ore-lead changed measurably during ore deposition. Present data imply that comparable variations exist elsewhere only among U-leads. This is one of many indications that J-leads and U-leads may have originated by somewhat similar geochemical processes.

This kind of exceptional lead, first discovered by Nier (96) in galena from Joplin, Mo., has been defined and named "Joplin-type" or "J-type" by plumboscientists at the University of Bern (76, 11). Such J-lead is mined in the major lead-zinc districts of the Mississippi Valley in tonnages so substantial that it constitutes 45 percent of present lead production in the United States, yet it has been found virtually nowhere else in the world. In interior North America the geographic distribution of J-lead so far known stretches

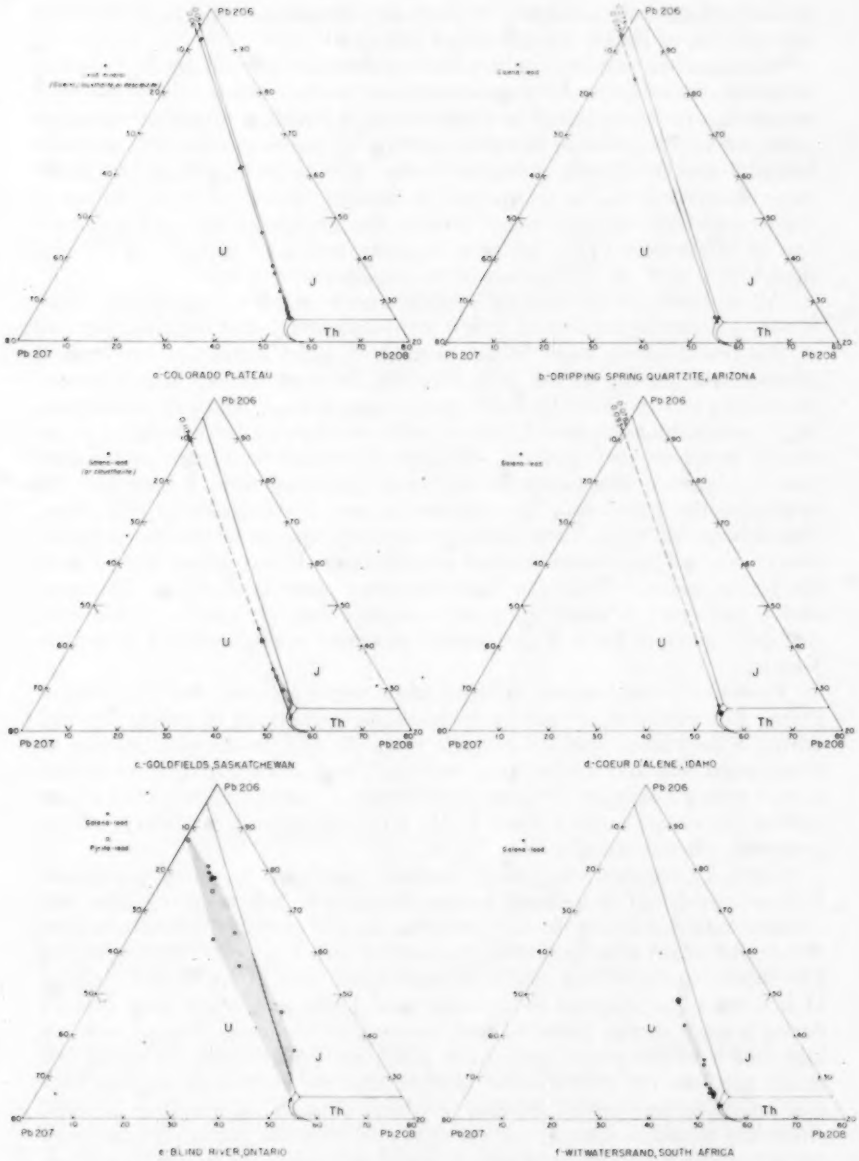


FIG. 17. Isotopic composition of lead from radioactive ore deposits. After Cannon, Stieff and Stern (29).

from the Folded Appalachians to the Uinta Mountains, and from Arkansas and Arizona to British Columbia and Ontario.

Most geologic occurrences of J-lead are lead-zinc ore deposits in Paleozoic sedimentary rocks, chiefly marine carbonate rocks. Some others are trace occurrences of J-lead galena in joints, cracks, or veinlets in similar carbonate rocks, or in Precambrian basement rocks that are now mantled (or might recently have been) with Paleozoic cover. It may be significant that all of these occurrences can be interpreted as deposits formed under conditions of low temperatures and pressures. Finally, though lead of this kind is ubiquitous in Mississippi Valley lead-zinc deposits, analogous deposits of "Mississippi-Valley-type" in Europe appear to contain ordinary lead.

All of these characteristics combined somehow fail to suggest any satisfactory geologic hypothesis of origin for J-lead and J-lead deposits, yet lead of this brand surely must be the product of some distinctive ore-forming process. At present we can only illustrate the great variety of geochemical processes that hypothetically might give rise to isotopic mixtures corresponding to compositions in area J. As a frame of reference for examining hypothetical processes and products, we have reproduced in Figure 18 the contoured frequency distribution of lead ores, borrowed from Figure 11. To emphasize the J-lead data the contours in area J are drawn as solid lines. The superposed heavy black arrow portrays the change in isotopic composition of ore-lead from inner to outer growth layers in our galena crystal from the Joplin region. These are data—the other symbols in Figure 18 represent a variety of schemes portrayed and reviewed here simply to illustrate that quite different kinds of geochemical processes can be imagined to explain J-leads.

Processes of two entirely different kinds might generate lead of J-composition: (1) evolution of lead by accumulating increments of radiogenic lead during a protracted span of geologic time, or (2) geochemical mixing of a radiogenic lead and another (e.g. ordinary) lead, instantaneously, or during a brief geologic episode. Figure 18 illustrates a variety of imaginary evolutionary processes (solid Curves I, II, III) and several imaginary mixing processes (dotted straight lines IV, V).

Curve I illustrates what would happen if we tried to evolve Joplin-lead from primeval lead in a closed system during 4.55 billion years. The true solution surely does not lie in this direction, for available data disclose no trends that might represent older products of such a system. Moreover, the Pb^{204}-content in such lead would be much lower than in Joplin-lead. Curve II is a schematic diagram to illustrate how Joplin-lead might have evolved during a much shorter period of time, starting, for example, from an ordinary lead half a billion years ago. Such a scheme comes closer to fitting the actual data, for the Pb^{204}-content is right, and the curve cuts through data that might be interpreted as older products of such an evolution process. According to such a scheme, our galena crystal from the Joplin region (heavy arrow) might have grown during a period of about 125 million years, as, for example, from late Paleozoic time to early Tertiary. A third evolutionary scheme (Curve III) calculated from actual measurements of lead, uranium,

and thorium in a particular specimen of rock (granite, Pitkeranta; from Fig. 16) merely illustrates how we might try to explain J-lead by geochemical extraction of total lead from some rock, at various times in geologic history. The composition of total lead in the granite is shown as measured now (0.0 at tip of curved arrow III), and as calculated backward in time half a billion years ago and more. Curve III demonstrates that if this granite were completely melted now, lead in the melt would be of J-type; and if this had

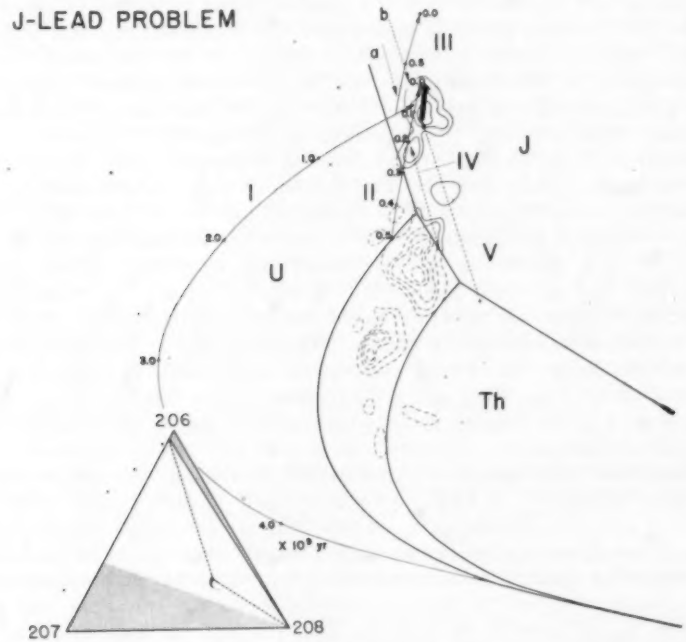


FIG. 18. Hypothetical schemes for deriving J-lead. I. Evolution during 4.55 billion years. II. Evolution during 0.5 billion years. III. Extraction of rock-lead (granite, Pitkeranta). IV and *a*. Mixing of ordinary lead with Pb^{206} (decay-product of segregated Ra^{226} and/or Rn^{222}). V and *b*. Mixing of leads from different minerals of granite (Essonville: plagioclase + zircon), as by partial extraction.

happened 500 million or more years ago, the resemblance to Joplin-lead would have been closer. Of existing data on rock-leads, the dozen nearest in composition to American J-lead ores are from such granites or from marine carbonate rocks. The test of these possibilities will be a study of rock-leads in the Paleozoic sediments and the Precambrian basement of the Interior Lowland in order to determine whether any of these rocks could have furnished the J-lead to form Mississippi Valley ores.

Next we can illustrate how some compositions of J-lead could be derived by simple mixing in various proportions of two leads of fixed compositions. Two such simple mixing schemes (IV and V) are illustrated by the dotted straight lines on Figure 18. Scheme IV represents mixing of an ordinary lead of zero model age (dotted arrow IV) with pure Pb^{206} (dotted arrow *a*). Such pure radiogenic Pb^{206} may someday be found in nature, inasmuch as intermediate daughter-products of the U^{238}-series do segregate to some extent, and must ultimately decay to Pb^{206}. Mixing of such ordinary lead with only 2¼ percent of pure Pb^{206} would produce J-lead at the tip of arrow IV, but its Pb^{204}-content would be higher than the Southeast Missouri ore-leads grouped there. A second mixing scheme (dotted arrow V) is based on actual measurements on constituent minerals of "Essonville granite" (126), the only crystalline rock of interior North America for which detailed lead isotope data have been published. Each mineral of this granite of course contains its own kind of lead so that partial extraction of lead from such a heterogeneous rock-system could give rise to mixtures of different compositions, depending on details of process. We illustrate only one of these many possibilities: mixing of lead from Essonville plagioclase feldspar (dotted line V) with lead from Essonville zircon (dotted line *b*). This scheme merely shows how lead in liquid produced by gradual melting of a mythical rock composed of these two minerals would change progressively if plagioclase were to melt first, followed by zircon. Admixture of five percent of zircon-lead with plagioclase-lead would yield lead of composition like Joplin-lead (tip of dotted arrow V). Here again, the problem is one that may be solved by study of lead in the country rocks, with emphasis on the more mobile fractions of rock-lead.

These five hypothetical mechanisms for combining radiogenic isotopes with pre-existing lead to yield mythical products in area J were offered in Figure 18 merely to illustrate the complexity of the problem, not as solutions. Some of them certainly are not feasible, whereas others might be permissive mechanisms for giving rise to such leads in nature. One further observation about origins of J-lead is that any system producing J-lead by long-term evolution would have to be poor in lead (or rich in both uranium and thorium). For instance, our four curves for evolution of ordinary lead (Table 1) represent systems with Pb/U weight ratios of 6.0 or more; but our three curves for evolution of J-leads (Fig. 18) are for systems with Pb/U ratios less than 3.0. If future research should prove that millions of tons of Mississippi Valley ore-lead emerged from some source environment poor in lead, then Joplin-lead will seem *anomalous* indeed.

This resumé is somewhat lengthy because we want to delineate the J-lead problem as clearly as can be done with evidence now in hand. We shall not try to guess exactly what further steps are most likely to guide us to a more detailed definition of the J-lead problem and ultimately to its solution. But we can suggest one further criterion that will be helpful for testing J-lead hypotheses as soon as the quality of analytical data can be sufficiently improved. Paragenetic isotopic variations observed within any J-lead deposit probably should plot parallel to the mixing line or evolution curve of the

process that produced the lead. The orientation of our heavy black arrow, in theory, should provide a test whether any one of the five schemes plotted on Figure 18 could explain the origin of our Joplin crystal—but the measurements in hand do not define the trend of variations with sufficient certainty.

SOME EMPIRICAL APPLICATIONS

Long before we have learned enough to answer all these questions about origins of ore deposits, we can with profit put to work some of the empirical associations and statistical variations observed in existing lead isotope data. The paper by Cannon, Stieff, and Stern cited above (29) was intended primarily to call attention to the opportunity to use isotopic evidence of U-leads as a tool in prospecting for uranium. For the prospector who finds a single sample of galena, pyrite, or similar nonradioactive ore mineral containing U-type lead, the chances are just about 50–50 that he is on the trail of a uranium deposit. The farther the composition of this single sample deviates from ordinary lead, probably the better his chances. By the time he has found a varied suite of U-leads like those in the top four diagrams on Figure 17, his chances of finding uranium have increased to something approaching 100 to 1. Here is one example. The paper referred to gave an illustration, reproduced here as Figure 19, showing three reported occurrences of exceptional leads from Ontario, one of J-type, two of U-type. One of the latter was described as (29):

> a suite of U-type galenas from small lead and zinc deposits [68] from the Thunder Bay region of the north shore of Lake Superior. This suite of analyses of U-type leads, recently reported and discussed at some length by Farquhar and Russell [59] presents a most difficult problem in evaluation. Our statistics suggest a high probability that such a suite of leads reflects association with uranium deposits. These data thus pose a most intriguing question, but we are inclined to temper this statistical evaluation with the knowledge that such leads can have other meanings and that wise judgment whether affiliations with uranium ores do exist must be based upon intimate knowledge of the deposits and their geologic environment.

Since that was written, we have learned that these small base-metal deposits (68) containing U-type leads evidently occur in just about the same beds of the Sibley series as do the radioactive, uranium-bearing nodules that Tanton discovered and described a few years ago (122). We have learned also that Russell (109, p. 88) in discussing these leads at the Third Conference on Nuclear Processes in Geologic Settings mentioned that "Prospectors have looked for uranium in this area and found traces of it. The background [i.e radioactivity] of some of these lead mines is up by a considerable factor over ordinary background."

Another application already being put to wide use is model dating—perhaps it is being used too widely, without enough discrimination. Dating ore deposits by model ages of lead in galena and other ore minerals can be justified, at present, chiefly for ordinary leads. Although model dating needs to be studied much more intensively, present odds imply that it can provide a useful approximation of real geologic age for a great majority of samples of

ordinary lead. Its greatest potential usefulness is in studying deposits in Precambrian terranes where definitive stratigraphic dating is not possible. Let us illustrate this view by citing the group of ordinary leads between the 1 and 2 b.y. isochrones on Figure 11. This group of data represents a great many lead deposits that occur in Precambrian host rocks. Out of approximately 75 deposits some are known to be of Precambrian age, most have true ages yet unknown, but not one of the group has been dated by stratigraphic evidence as definitely younger than Precambrian. For any single occurrence of ordinary lead of this composition, therefore, statistical odds appear to be greatly against the deposit being of Paleozoic or younger

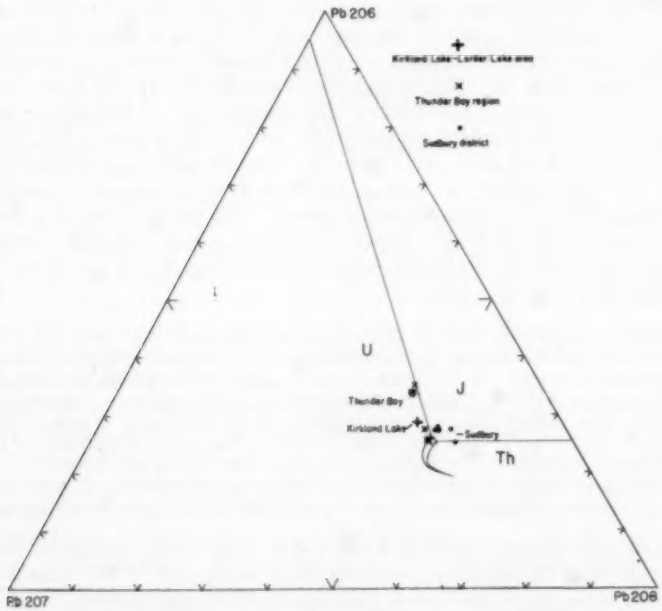


FIG. 19. Some exceptional leads from Ontario. After Cannon, Stieff, and Stern (29).

age. This group includes many analyses of Coeur d'Alene ore-lead, from deposits formerly assigned to a Cretaceous origin. This assignment is now in question since lead-uranium age of uraninite has been found to accord with the Precambrian model age of galena. The prospector who adds this possibility to his kit of working hypotheses may have an advantage over his competitors, but he should always remember that a Precambrian lead-ore deposit can be dissolved, transported, and reprecipitated in Cretaceous time, theoretically without changing the isotopic composition of the lead. As a second illustration, we can cite an example of immediate application of lead

isotope data in geologic exploration. After analysis of a galena-lead from a Precambrian gold deposit at Atlantic City, Wyoming, disclosed a model age of 2.8 billion years—by far the most primitive lead known in the United States (20)—the rocks of the region were sampled and discovered by a variety of dating methods (25, 40, 62) to include extremely ancient Precambrian rocks with apparent ages in the range between 2.0 and 3.05 billion years.

A final example is the practical use that could be made immediately of relationships that have been observed between isotopic composition of lead and size of deposit. The most striking relationship we have observed so far in this regard is that leads from major sulfide deposits conform to our narrower evolution model (dashed lines, Fig. 10) much more closely than do leads from minor deposits. If we exclude known radioactive deposits and J-leads from our calculations, a mineral prospect found to have lead composition inside this narrow model has 3 times better chance of developing into a major sulfide mine than one whose lead falls outside to right or left. And inside this narrow crescent a prospect whose lead falls above the 2 b.y. isochrone has 3 times better chance of becoming a major sulfide mine than a prospect whose lead falls below this isochrone (i.e. older model age). Within this favorable part of the ordinary-lead field, between zero and 2 b.y. isochrones, one in six of all localities sampled (i.e. mines, prospects, and trace occurrences) is a major mine. And the prospector who finds a sample that plots in the most favorable part of this field would appear, *on the basis of these data,* to have better than an even chance that he has discovered a major ore body. We have other bits of evidence suggesting that better lead isotope analyses will reveal additional correlations of isotopic composition with size of deposit.

CONCLUSION

The existing lead isotope data reviewed in this report leave much room for improvement both as to quality of analytical results, as well as quality and quantity of geologic sampling. Wherever we have illustrated our interpretations by translating the data into specific numbers involving evolution of lead, model age, relationships between various deposits, or guides for prospecting, we know that these numbers will be changed by better data. The general tenor of our conclusions, however, we believe to be valid despite the imperfections of the data. For the future we predict that better data will make it possible to sharpen these and to draw many new generalizations that have not yet been detected.

The future of lead isotope research is going to depend most of all on the success that can be achieved in integrating skills and knowledge from many fields of science. For we are simply studying the physical products of radioactive decay as a unique tool to improve our knowledge of the geochemistry of lead enough to solve a wide variety of important geologic problems. Cosmologists, now hard at work on the origin of the elements and nuclide abundances, will eventually help us learn about the isotopic composition of lead through the early stages of earth-history. Physicists and chemists, working together, have been making rapid strides in improving the quality

of lead mass spectrometry and in overcoming the hazards of lead-contamination in processing samples for lead isotope study. But lead isotope analyses must be made still more accurate—and less expensive—and techniques for extracting traces of lead from rocks without contamination must be further refined, for rock-leads are the key to lead isotope geology. The time has come for geologists to face up to the fact that in lead isotope studies the weak link has been geology. Too few geologists have devoted time to lead isotope research. The geologist has not yet assumed his proper share of responsibility in defining the geologic problems, planning the attack on them, sampling the earth so as to learn the crucial facts, and interpreting and applying the results. It is particularly important for the geologist to insure that all pertinent geologic information from every quarter is brought to bear. This premise is so fundamental that we wish to leave it as our closing thought, particularly as we could not give it suitable emphasis in this paper. Many more geologists must make the effort to understand the simple principles that underlie lead isotope geology, and the complexities of lead isotope interpretations.

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U. S. GEOLOGICAL SURVEY,
DENVER, COLO.,
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TEPHROITE IN CALIFORNIA MANGANESE DEPOSITS

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ABSTRACT

Recent studies of manganese deposits and mineral specimens in the Sierran belt of sedimentary rocks as well as in the Klamath Mountains to the north and in the Rand Mountains to the south, have shown the presence of tephroite, the orthosilicate of manganese (Mn_2SiO_4), at numerous localities. Earlier studies of these deposits have shown that the original layered deposits of carbonate and hydrous silicates of manganese have been widely altered by metamorphism to spessartite ($Mn_3Al_2(SiO_4)_3$), rhodonite ($MnSiO_3$), and piedmontite ($Ca_2(Al,Mn''',Fe''')_3Si_3O_{12}(OH)$). Recent work shows that layered manganese oxides also were present in the original sedimentary rocks. It shows also, that tephroite has formed widely in the original assemblage of carbonate, silicate, and oxide of manganese; in several localities, a little alleghanyite ($2Mn_2SiO_4 \cdot Mn(OH,F)_2$) has been formed. Rhodonite, spessartite, and piedmontite uniformly follow the tephroite; in places, bementite and neotocite are present. In one deposit a little pyroxmangite ($(Mn,Fe,Ca)SiO_3$) has been noted and in another, some crystals that are probably pyrophanite ($MnTiO_3$), not yet recorded in the United States.

By contrast, the restudy of large collections of material from deposits in sedimentary rocks of the Franciscan formation in the Coast Ranges indicates the tephroite is very uncommon; it has been recognized with assurance at only one locality—Alum Rock Park, Santa Clara County. In the Coast Ranges, rhodonite and spessartite, the high manganese garnet, are very uncommon. The assemblages of manganese silicates indicate that the layered deposits of manganese minerals in the Sierra belt have been metamorphosed to a higher degree than those of the Coast Ranges.

This review also shows the presence of axinite, the boro-silicate of aluminum, calcium, and manganese, in three deposits.

INTRODUCTION

DURING the war period, 1917–1918, most of the known manganese deposits in California were examined by geologists employed by the California Council of Defense under the leadership of Prof. George D. Louderback of the University of California. Most of the field examinations were made by E. F. Davis, A. O. Woodford, F. S. Hudson, N. L. Taliaferro, and R. R. Morse. The program of work was carried out in cooperation with the U. S. Geological Survey and Stanford University, and a summary report was published in Bulletin 125, by the California Division of Mines (4) The interpretation of the modes of origin of the deposits in two provinces, the Coast Ranges and the Sierra Nevada, appears in two reports, also in Bulletin 125, written respectively by N. L. Taliaferro and F. S. Hudson, and N. L. Taliaferro.

The program of field study of the manganese deposits of the State was continued during the second war, 1939–1945, by a group of geologists of the U. S. Geological Survey under the general supervision of Parker D. Trask. This work yielded another report (11) which is largely devoted to detailed descriptions of geological features and interpretations of explorations at 675 localities or deposits of manganese minerals. At most of the localities, as explorations have been meagre, only the common oxides of manganese have been found and these are interpretated as supergene in origin, derived by the decomposition of several carbonates and silicates of manganese. At only about 100 deposits have explorations revealed the nature and geological relations of the unweathered minerals.

As a part of a program of review of the manganese deposits of the United States, one of the present authors (D.F.H.) has recently reviewed the literature and re-examined numerous manganese deposits in California in the hope of further clarifying problems of their modes of origin. In addition to his own collections of specimens, this author has had access to those made by other members of the Geological Survey, especially those made by Ivan F. Wilson in the Sierra Nevada and by Frank S. Simons and Max D. Crittenden in the Coast Ranges and Klamath Mountains.

It is not the purpose of the authors to make a comprehensive review of the mineralogy or geologic features of the manganese deposits of the Sierra Nevada belt, the Klamath Mountains, and the Coast Ranges. It is the purpose, rather, to record the widespread occurrence of tephroite in deposits of

the Sierra Nevada belt and the Klamath Mountains and to indicate its significance in the genetic history of the deposits.

ACKNOWLEDGMENTS

In this study, the specimens from Siskiyou, Humboldt, Trinity, and Calaveras Counties examined, were collected by Ivan F. Wilson and Parker D. Trask, then with the U. S. Geological Survey; the deposits in Butte, Nevada, Amador, and Mariposa Counties were examined by D. F. Hewett; and the deposits in Kern County were examined by C. W. Chesterman and B. W. Troxel.

In the preparation of this report, the authors wish to acknowledge the benefit of discussions of some of the problems with their associates at Menlo Park and San Francisco. X-ray diffraction analyses of four specimens of tephroite have been made by Robert A. Gulbrandsen and Max D. Crittenden of the Geological Survey. From time to time during the laboratory studies, Donald E. Lee of the Geological Survey at Menlo Park, having intimate knowledge of manganese minerals and the special techniques used in their identification, has examined some of the specimens and thin sections, and confirmed the identification of several minerals; he is responsible for the recognition of pyrophanite in the specimens from the Manga-Chrome mine. The photographs that appear here were made by Hal G. Stephens of the Geological Survey.

TECHNIQUES

In studying the minerals in ores, with concern for their paragenetic relations, the authors have found it advisable to adopt the following techniques. During the field examination of a deposit, large specimens, generally 4 to 10 inches in diameter, are carefully selected so as to show the maximum number of minerals and the range in their relations. In the laboratory, the large specimens are sawed so that one or more plane surfaces will further reveal the maximum number of minerals and their relations. If the specimen is made up largely of carbonates and silicates, it is treated cautiously with hydrofluoric acid. The silicates will be selectively etched; garnet and quartz are the most resistant to attack, rhodonite is readily etched, but tephroite, alleghanyite and the hydrous silicates are most rapidly attacked. By contrast, carbonates containing manganese become coated with a thin layer of fluorides which prevents further attack. As the fluorides are nearly white they appear in sharp contrast with the gray, pink and brown silicates. As most specimens of tephroite are gray to light brown, such areas of the specimen may now be tested for gelatinization. If the test is positive, small blocks, about 1 by 2 inches, are sawed for thin sections. Commonly, tephroite may be fairly proven by immersion in oils and in thin section by optical tests, but where positive identification is advisable, samples are tested by X-ray diffraction methods.

This procedure has been followed in the examination of many specimens during this inquiry; experience has shown that if random chips are chosen for thin sections, tephroite and other important minerals may be missed.

MANGANESE DEPOSITS IN CALIFORNIA

From the field and laboratory work that have been done by many persons since 1917, the many deposits in the State fall rather readily into four belts or areas within which the known deposits are concentrated in several rock or formation units.

1. In the Coast Ranges, extending from the Transverse Ranges in Santa Barbara County on the south, 500 miles northwest to a fault that separates the Coast Ranges in Humboldt County from the Klamath Mountains, on the north, all of the known deposits, about 400, lie in the Franciscan formation of Late Jurassic to Late Cretaceous age (4).

2. In the Klamath Mountains, a rugged area about 50 by 80 miles, about 85 manganese deposits are known. The host rocks are both metamorphic and metasedimentary that range in age from early Paleozoic to Jurassic. Neither the manganese deposits nor the host rocks have been studied sufficiently to permit confident conclusions concerning their geologic relations.

3. On the Western slope of the Sierra Nevada, extending from the Transverse Ranges and the Garlock fault on the south to Plumas County on the north, about 120 manganese deposits have been examined. From present knowledge, it appears that most of these deposits lie in the Calaveras formation of late Paleozoic age and most of the remainder lie in the Amador group of Middle and Late Jurassic age (4).

4. The remaining deposits, about 100 in number, lie in the southeastern third of the State. Most of these are found in Tertiary sedimentary rocks and volcanic rocks and have thus far yielded only oxides of manganese. Several deposits are known in the Rand schist of Precambrian age and one, the Big Indian near Randsburg, contains the same assemblage of minerals known in some deposits in the Sierra Nevada.

Concerning the manganese minerals in the Franciscan sedimentary rocks, Taliaferro and Hudson (4) state:

> p. 237, Probably the most abundant material in the original deposits (syngenetic) and certainly the one which yields the best oxides, is manganese carbonate, usually in a very finely divided state. The other material, nearly as abundant as the carbonate, and making up the great bulk of several deposits, is brown manganiferous opal.
>
> p. 239, Almost as abundant as manganese carbonate as an original syngenetic substance, is a brown manganiferous opal of variable composition. Although some deposits are essentially made up of this type of material, variable amounts of manganese carbonate are always present.

In discussing the possibility of hydrothermal alteration of deposits in the Franciscan, Taliaferro and Hudson (4) state:

> p. 268, Hydrothermal alteration may produce striking mineralogical changes but it does not appreciably alter the form of the ore bodies—there are some deposits that clearly owe their present mineral assemblage to hydrothermal activity.

With reference to the uncommon assemblage of manganese minerals determined by Rogers (8) in the Alum Rock block, Santa Clara County, (hausmannite, pyrochroite, rhodochrosite, tephroite, ganophyllite, and barite.) Tali-

aferro and Hudson state: p. 268, "The unusual assemblage of minerals indicates that it is the result of rather high-temperature hydrothermal action, possibly complicated by contact metamorphism."

On the basis of the recent examination of about a dozen manganese deposits in Franciscan sedimentary rocks in Santa Clara, Lake, Mendocino, Trinity, and Humboldt Counties, and the subsequent study of many polished and thin sections, one of the writers (D.F.H) should record that this work confirms most of the interpretations of genesis made by Taliaferro and Hudson. This recent work indicates that in most localities, hausmannite has formed by replacement of layered manganese carbonate. At one deposit, however, the Blue Jay, Trinity County, it may have been formed by the alteration of an original layered oxide. As the record for deposits in Franciscan sedimentary rocks stands at present, tephroite has been assuredly recognized only at Alum Rock, Santa Clara County.

Concerning the manganese minerals in deposits in the Calaveras formation, Taliaferro (4) states:

> p. 292, It is believed that the manganese was originally deposited as a chemical sediment, in the form of the carbonate or as a manganiferous silica gel, or colloid, or often as a mixture of the two, and that the denser silicates have been formed by the metamorphism of these substances.
>
> p. 291, This material (the existing unweathered "primary" minerals, in contrast with the "original" material) consists of manganese carbonate, partially recrystallized manganiferous opal, rhodonite, a manganese garnet, probably spessartite, and very minor amounts of other manganese minerals, such as manganiferous amphibole.
>
> p. 331, Because of the very close and constant association of manganese deposits with cherts, not only in the Sierra Nevada but also in the Coast Ranges . . . it is believed that the manganese in deposits of this type was derived from essentially the same source as the silica forming the cherts. *** It is believed that these more massive chert lenses represent a more rapid local addition of silica to the sea water . . . this is the only evidence that favors the theory that the source of both the manganese and the silica was from submarine springs derived from the volcanics rather than from the leaching of the volcanics.

Finally, with reference to the modes of occurrence of manganese in the rocks of the Amador group, Taliaferro (4) states:

> p. 324, Just as in the case with the Franciscan deposits, manganiferous opal (neotocite) and manganese carbonate, usually containing a considerable amount of lime, are the original chemical deposits from which all the other manganese minerals have been derived. * * * The original manganiferous opal has been largely altered to fibrous and granular aggregates of hydrous manganese silicates of the bementite type, similar to those in Franciscan deposits. * * * The minerals that have been developed by metamorphism and hydrothermal alteration are rhodonite, recrystallized manganese calcium carbonate, spessartite, mangano-calcite, mangano-siderite, and piedmontite, the manganiferous epidote.
>
> p. 325, Veins of secondary rhodonite and of rhodonite and quartz are common.

The work that has been done recently by the authors tends to confirm the earlier interpretation of the mode of origin of the layered manganese minerals in the sedimentary rocks of the Calaveras formation and Amador group. Recent work, in only a few deposits, however, indicates that in addi-

tion to the layers of manganese carbonate and manganese opal, there are also layers of manganese oxide, now represented by the oxide, hausmannite. Also, as shown in the following pages, the orthosilicate, tephroite, has been found in ten localities in the Klamath Mountains and Sierra Nevada in large quantities in several deposits.

TEPHROITE

General

The orthosilicate of manganese (Mn_2SiO_4) is not a common mineral in the United States. It was reported more than 100 years ago in Vermont, New Hampshire, Massachusetts, Rhode Island, and Connecticut. Only at West Cummington, Hampshire County, Massachusetts is it known in abundance (D.F.H.). It is locally abundant at Franklin Furnace, New Jersey (6) and in recent years, it has been recognized in abundance at Bald Knob, Alleghany County, North Carolina (9). It has been found in abundance by one of the writers (D.F.H.) at the Dorn mine, Abbeville County, South Carolina. Also, it has been reported from the Kothman Tract, near the Spiller mine, Mason County, Texas (10).

In the West, tephroite was observed in an uncommon assemblage of manganese minerals in the Sunnyside vein, Eureka Gulch, San Juan County, Colo. (1). Park (7) records the presence of tephroite with other silicates and some oxides at the Apex mine, Mason County, Washington. One of the writers (D.F.H.) recently observed abundant tephroite, in part altered to rhodonite, at the Shamrock mine, Jackson County, Oregon.

California

In the latest edition of "Minerals of California," Murdoch and Webb (5) report the presence of tephroite in only two localities in the State, Santa Clara and San Diego Counties. In both localities, the mineral was found in boulders, the exact source of which is not known. The boulder from Alum Rock Park, near San Jose, contained the oxides, hausmannite, pyrochroite, and psilomelane; the silicates, tephroite, alleghanyite and ganophyllite; the carbonate, rhodochrosite; and the chloride, kempite (8). Tephroite is not recorded in either of the two summary reports on California manganese deposits (4, 11).

By re-examining collections of manganese minerals made during the War, 1941–45, and by field examination at six localities in the State, tephroite has been positively identified at eleven localities by the authors. Tests of material from two other localities indicate its presence. The mineral is probably present widely in the Klamath Mountains and Sierra Nevada.

Siskiyou County.—At the National Defense claim, sec. 16, T. 40 N., R. 10 W., Mount Diablo meridian, explorations reveal a lens of quartzite (meta-chert) in quartz-mica schist that is probably pre-Silurian in age (3). In the middle of the quartzite (meta-chert), there is a lens of gray material which is the source of specimens collected by Wilson (11). The texture

shows a range from fairly coarse granular to finely porcellanous. Recent tests of polished sections, confirmed by X-ray diffraction analysis, show that the gray material with fine texture is nearly pure tephroite and that the granular material is largely manganese carbonate. Rhodonite is reported in the deposit but none is present in the specimens examined.

Humboldt County.—A specimen from the Queen's Peak manganese deposit in sec. 34–35, T. 4 S., R. 1 E. Humboldt meridian, near Shelter Cove, submitted to the California Division of Mines, has been examined. According to the geologic map prepared by Irwin (3), the locality is underlain by rocks of the Franciscan formation. The specimen, weighing about 10 pounds, is mottled light and dark gray. The light gray areas are a manganiferous carbonate and the darker areas gelantinize when treated with hydrochloric acid. No tephroite is present, however, in the only thin section examined.

Trinity County.—Work by several geologists of the U. S. Geological Survey during 1942 showed that a deposit explored by the Manganese Queen mine in sec. 26, T. 30 N., R. 12 W. Mount Diablo meridian, is a lenticular body of manganese minerals, about 140 feet long and 8 feet thick on the border of a persistent bed of chert where it overlies sandstone and shale (11). These sedimentary rocks are interpreted as Triassic or older, possibly equivalent to the Applegate group of southwestern Oregon (3). The lens contains numerous manganese minerals, rhodonite, bementite, rhodochrosite, and possibly hausmannite and braunite. Parts of a specimen gelatinize when treated with hydrochloric acid but no tephroite was identified in a single thin section.

The Lucky Bill (Old Bill) prospect lies in sec. 9, T. 28 N., R. 11 W., Mount Diablo meridian, about 10 miles southeast of the Manganese Queen mine. According to Trask (11), the mineralogy and geologic environment of the deposit closely resemble those at the Manganese Queen mine where much more exploratory work has been done. Specimens collected by I. F. Wilson in 1942 have been examined recently in polished and thin sections. The color of the specimens ranges from light to dark gray and the texture from coarse to very fine. Thin sections show that the material is largely carbonate and tephroite; some hausmannite is present but no rhodonite or bementite that are reported by Trask (11). As at the National Defense claim in Siskiyou County, the fine-grained light-gray material is largely tephroite.

Butte County.—Specimens of manganese minerals collected by I. F. Wilson from the Binet prospect in sec. 34, T. 20 N., R. 7 E., Mount Diablo meridian, about one mile north of Clipper Mills, have recently been examined in polished and thin section. One specimen of dense light-gray rock is largely finely granular tephroite and carbonate which are locally cut by veins of rhodonite and locally replaced by bementite.

During a visit by one of the writers (D.F.H.) to the area during September, 1959, the Binet prospect could not be located but he was able to visit the Bear Canyon mine in the S½ sec. 27, T. 20 N., R. 7 E., where the principal work is a tunnel, now caved. Most of the material on the dump

is fine-grained rhodonite rock but in one large block, there are unreplaced areas of fine-grained gray rock which, in thin section, are shown to be largely manganese carbonate with sporadic grains of tephroite. In and near the areas of rhodonite, there are aggregates of minute crystals of spessartite. The host rock is micaceous shale of the Calaveras formation.

Nevada County.—The Manga-Chrome (Duggan) mine lies near the south border of sec. 17, T. 14 N., R. 8 E., Mount Diablo meridian, about 10 miles north of Auburn. The deposit was explored during both wars and has yielded several hundred tons of oxide ore. The principal work is a trench about 350 feet long and 25 feet deep that lies 100 feet east of Wolf Road. As the trench is now partially filled with waste and overgrown with shrubs, the only material available for study is the large dump north of the trench. On the basis of an examination during 1942, I. F. Wilson has described the workings and local geological features (11, p. 162–164). Wilson presents a stratigraphic section of the rocks at the trench, thin-bedded chert, phyllite, slate, and diabase sills which are probably a part of the Amador group. The area was visited by one of the authors (D.F.H.) during September, 1959.

Examination of ten large polished and etched specimens and of nine thin section shows that most of the material on the dump is made up of three minerals, hausmannite, manganese carbonate, and tephroite. Some large blocks are nearly pure hausmannite, in part massive and in part thinly layered; in other blocks the grains and crystals of hausmannite are imbedded in finely crystalline carbonate. In most of the large blocks on the dump, the hausmannite-carbonate rock is partially or largely replaced by plumose aggregates of granular tephroite; in addition to its optical properties in thin section, tephroite has been confirmed by X-ray diffraction analysis. Figure 1 shows a section of the rock sawed normal to the bedding; the details of the mineralogy were studied in three thin sections, representing the entire cross section of the block. The upper third is an intimate mixture of grains of hausmannite and manganese carbonate, through which there are dispersed grains of tephroite and barite, largely concentrated along the bedding. This part of the block is cut by oblique veins of tephroite and barite. The middle third of the block contains one thick and several thin, layered masses of coarsely crystalline tephroite which has replaced the hausmannite-carbonate material; in this part of the block there are also oblique veins of tephroite and barite. In the lower third of the block, four fairly definite layers are recognized. At the top is a thin layer of dark fine-grained isotropic silicate (neotocite?); under this is a layer of hausmannite-carbonate partially replaced by granular tephroite; then follows a layer of fine-grained silica (chert?). The lowest layer is largely a fine-grained mixture of hausmannite and carbonate, sporadically replaced by lenses of tephroite; the lower part of this layer is now largely bementite in which there are minute well-preserved radiolaria; nearby, the bementite contains minute crystals of garnet. This part of the rock also contains oblique veinlets of barite.

To the writers, this block was originally alternating (1) layers of manganese oxide and carbonate, probably with some dispersed silica; (2) layers of hydrous silicate of manganese (opal or neotocite?); and (3) layers of

silica. This study has not revealed large cross-cutting veins or fractures along which solutions could bring in exotic manganese or silica to the layered sediments. The material now available for study seems to represent the product of alteration by burial alone, having been buried to the depths that would yield temperatures high enough to induce reactions in the sedimentary materials. It seems significant, however, that even though the layers of carbonate and oxide of manganese with some local silica were largely altered

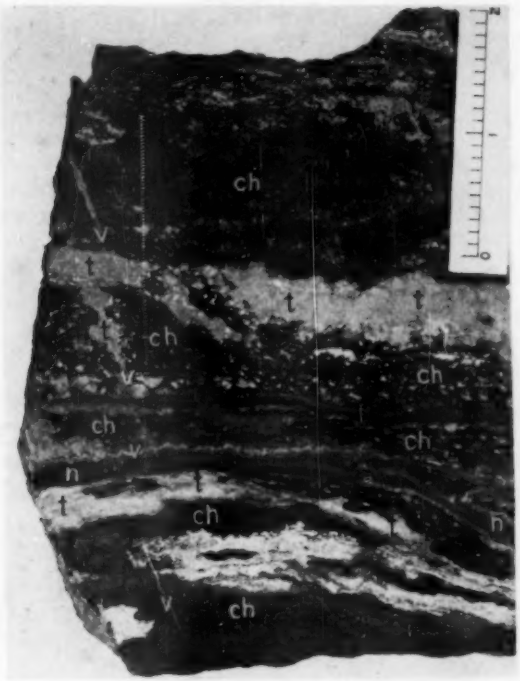

FIG. 1. Specimen from the Manga-Chrome mine, Nevada County, Calif. Shows successive layers of manganese carbonate-hausmannite (ch); neotocite (n) sporadically replaced by tephroite (t); and veinlets of tephroite and barite (v). The lowest dark layer is largely bementite that contains well-preserved radiolaria.

to tephroite, several layers of both fine-grained silica and manganese silicate remain unaffected. If there had been a vigorous movement of water transverse to the bedding, these layers could not have survived.

Several large blocks of rock on the dump, largely layered oxide, carbonate, and silicate of manganese, contain also sporadic angular blocks of dark fine-grained igneous rock, probably basalt, the borders of which are corroded and replaced by carbonate. These fragments of igneous rock, considered with

the sills (flows?) of diabase, indicate the association of the manganiferous sediments with vulcanism.

The Smith prospect lies near the center of sec. 32, T. 14 N., R. 8 E., Mount Diablo meridian, about 3 miles south of the Manga-Chrome mine. It is accessible by dirt road that leaves State Highway 49 about 9 miles north of Auburn. The deposit is explored by a deep trench about 25 feet long which

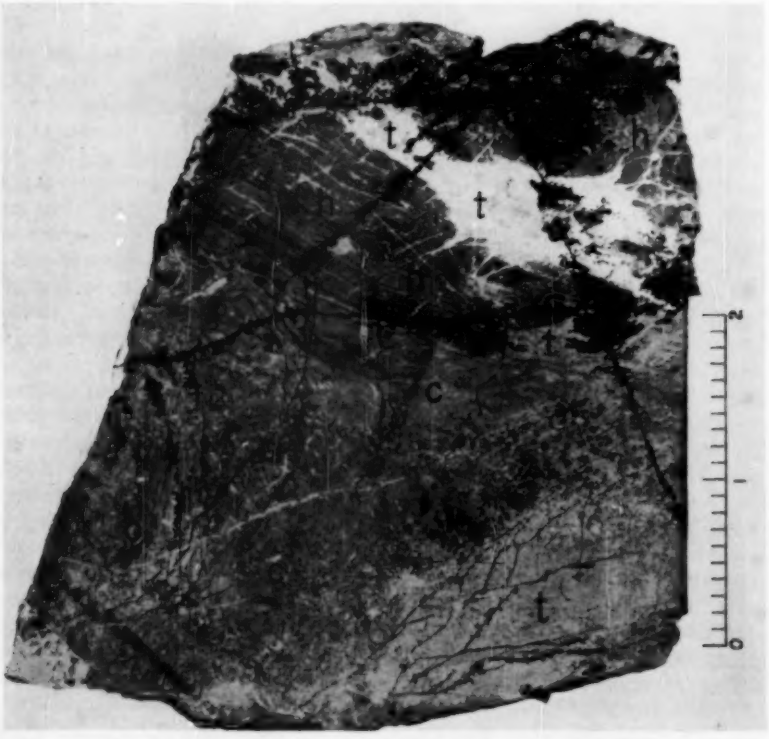

FIG. 2. Specimen from Smith prospect, Nevada County, Calif. Shows a layer of crystalline manganese carbonate (c) (below) and a layer, largely hausmannite (h) (above), both sporadically replaced by tephroite (t).

extends eastward to a shaft about 15 feet deep, now filled with waste. This shaft exposes a vertical bed of fine-grained gray carbonate about 2 feet thick, on one wall of which there is a bed of nearly pure hausmannite about 6 inches thick. In polished sections, the carbonate is very fine grained and without layering but the hausmannite shows persistent thin layers (fig. 2).

In thin section, the carbonate contains patches of gray granular tephroite and the two are cut by sporadic veinlets of tephroite with some bementite.

The bed of carbonate is overlain and underlain by a foot or more of rhodonitic chert which merges outward with the host rock, layered chert. According to Taliaferro (4) and Wilson (11, pp. 167–168), the cherts are part of the Amador group. Figure 2 shows thinly laminated hausmannite and granular carbonate replaced by lenses of granular tephroite.

Amador County.—The Germolis prospect lies on a low spur that forms the southern border of the south fork of Dry Creek, opposite the Germolis ranch house in SE¼ sec. 9, T. 7 N., R. 11 E., Mount Diablo meridian, about 3 miles south of Fiddletown. According to Wilson (11, p. 30) the prospect explores a zone of manganiferous meta-chert, 5 to 6 feet wide, within which there are pockets (nodules?) of manganese minerals 3 to 4 inches wide. The zone is a part of a much thicker zone of meta-chert and shale interpreted by Wilson as being a part of the Calaveras formation. In 1959, the face of the cut was covered by local debris but specimens from the dump have been sawed, polished, and etched and studied in thin section. Manganese minerals, largely carbonates and silicates, form flat nodules 4 to 6 inches in diameter and 1 to 3 inches thick; these are wholly enclosed in dark-gray meta-chert (Fig. 3). Nearby there are layers of granular spessartite overlain and underlain by meta-chert. No cross-cutting veins of manganese carbonate or silicate have been observed near the nodules. The cores of the nodules are largely pale-pink manganese carbonate in the midst of which there are aggregates of darker grains of tephroite and alleghanyite; the cores are completely surrounded by zones of pink rhodonite, ⅛- to ¼-inch thick and these zones, by another of quartz grains and sporadic aggregates of spessartite crystals.

In the absence of veins of manganese minerals cross-cutting the meta-chert that might be channels of access for exotic manganese, it is concluded that the nodules were originally largely carbonate with some silica, deposited in the midst of sedimentary silica and that the existing silicates, alleghanyite, tephroite, rhodonite, and spessartite, have arisen out of the reaction between carbonate and silica under the influence of thermal metamorphism. In other words, all of the manganese in the zone was indigenous in the original sediments. The orthosilicate, tephroite, has formed in the carbonate nodule and is protected from the silica in the meta-chert environment by the thin zone of the metasilicate, rhodonite.

The Lubanko prospect lies a mile east of the Germolis prospect, in the valley of the south fork of Dry Creek, in SE¼ sec. 10, T. 7 N., R. 11 E. Mount Diablo meridian. The specimens examined were collected by I. F. Wilson in 1942 who reported (11, p. 31), that nodules and lenses of manganese carbonate are dispersed in beds of meta-chert that are probably a part of the Amador group.

One specimen is a flat nodule in which a core of carbonate and tephroite is completely surrounded by a zone of radiating crystals of rhodonite about a quarter of an inch thick. In one thin section, tephroite grains form about 50 percent of the core; alleghanyite, about 15 percent; and carbonate, about 35 percent. Here, as at the Germolis prospect, the manganese minerals form nodules which are isolated in the host rock, meta-chert.

Mariposa County.—The Caldwell (Daly) mine lies in the NE¼ sec. 14, T. 3 S., R. 15 E., Mount Diablo meridian, about 6 miles southwest of Coulterville and 1 mile north of the valley of Merced River. Fortunately, bedrock is well exposed in the area; Taliaferro presents (4, p. 322) the details of a stratigraphic section of the Hunter Valley cherts of the Amador group in which the position of the ore zone of the Caldwell mine is indicated. Also, an inclined shaft on the Caldwell property, 57 feet deep, encountered unoxidized material. The dump contains a wide variety of materials and numerous polished and thin sections of specimens have been studied.

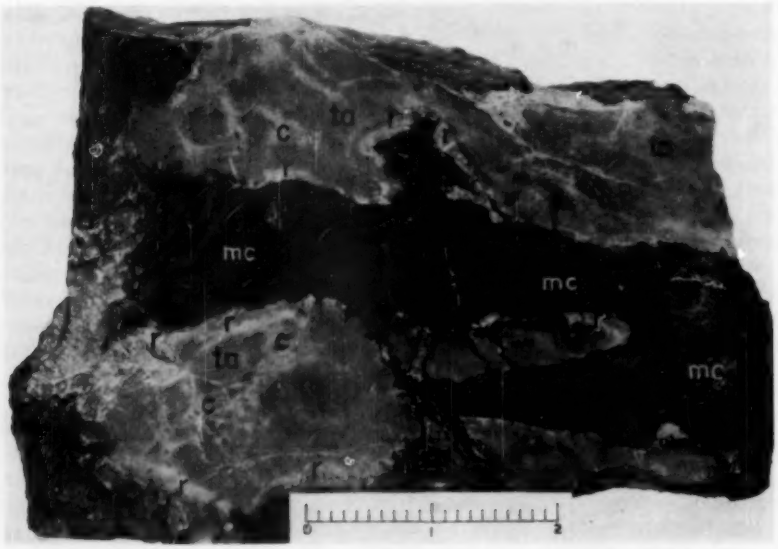

FIG. 3. Specimen from Germolis prospect, Amador County, Calif. Shows nodules of manganese carbonate in matrix of meta-chert (mc) (black). Nodules are now sponge of tephroite and alleghanyite (ta) (dark gray) in midst of manganese carbonate (c) (medium gray) surrounded by a thin layer of rhodonite (r) (light gray).

The Caldwell shaft explored a thick bed of coarsely crystalline manganiferous carbonate, interlayered with thinner layers of hausmannite and manganese silicates; some layers are wholly minute crystals of piedmontite and others are rhodonite. One specimen contains a thin layer of minute barite crystals. From the work done on the specimens from this shaft, it seems quite clear that before burial and metamorphism, the ore zone was made up of alternating layers of manganiferous carbonate, oxide, and silicate. In the ore zone, probably in the hanging wall, there is a bed of green volcanic breccia considerably altered to piedmontite.

About 500 feet southwest of the Caldwell shaft, the ore zone is exposed

in a shallow trench about 100 feet long. In the trench, only a little carbonate remains and specimens show its progressive alteration to hausmannite, to tephroite, and to rhodonite. In Figure 4, the dark areas are wholly minute crystals of hausmannite; the dark-gray veins that envelop the hausmannite are plumose aggregates of tephroite crystals and the light-gray areas are rhodonite. There are a few inconspicuous veinlets of late bementite. The specimen shows one area of coarse crystals of barite that have probably grown at the expense of the barite in thin inconspicuous layers.

FIG. 4. Specimen from Caldwell mine, Mariposa County, Calif. Shows remnants of granular hausmannite (h) (black), surrounded by granular tephroite (t) (medium gray), and this by rhodonite (r) (light gray), all of which have replaced crystalline manganese carbonate (c); cluster of radiating crystals of barite (b).

Calaveras County.—The Kellogg mine is located in sec. 4, T. 2 N., R. 12 E., Mount Diablo meridian, about 7 miles south of Altaville. Several openings explore lenses of manganese minerals in chert that is probably a part of the Amador group (11, pp. 45–46). A single specimen collected by Wilson in 1942 shows layers of dense brownish-gray material that resembles some chert but a thin section shows that it is largely carbonate with clusters of grains of tephroite, in process of replacement by finely fibrous material that is probably bementite.

Kern County.—The Big Indian manganese deposit lies in sec. 11, T. 30 S., R. 40 E., Mount Diablo meridian, in the Rand Mountains, about 2 miles

south of Randsburg. The principal exploration is an opencut about 50 feet long which attains a depth of 6 feet at the north end; other trenches explore the northwestern extension of the zone for 200 feet (11, 1950, p. 84).

In the area of the Big Indian deposit (5), the host rock is Rand Schist of Precambrian age, which is largely layered chloritic schist with thin layers

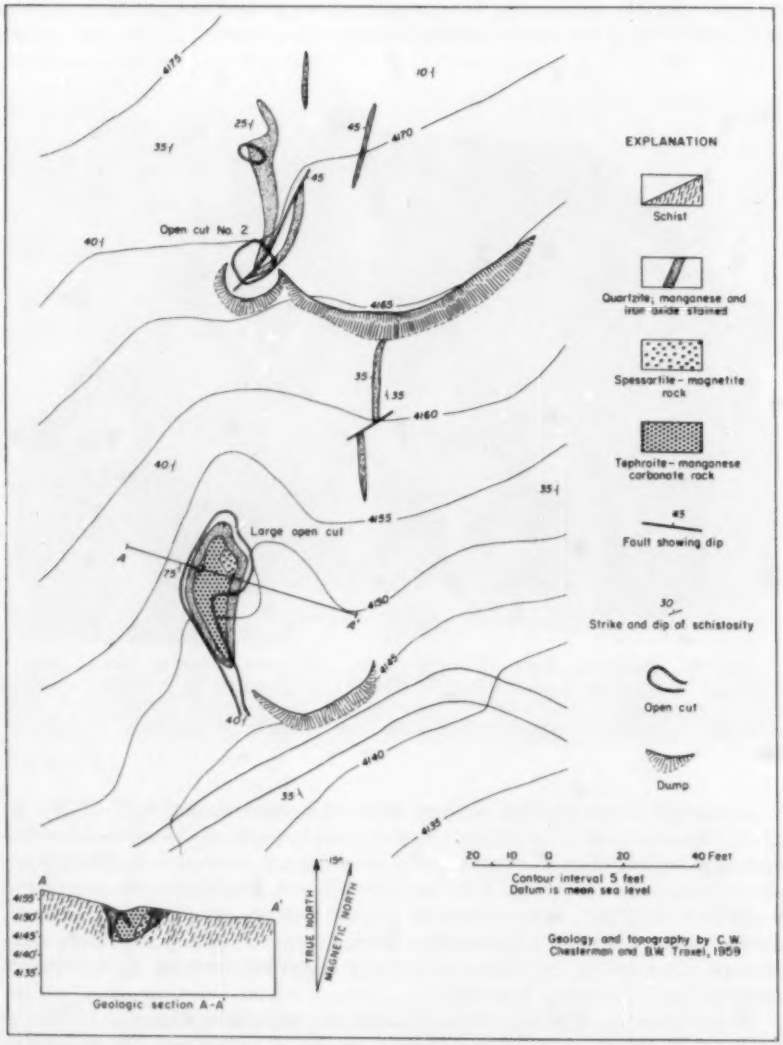

FIG. 5. Geologic map of the Big Indian manganese deposit, Kern County, Calif.

of quartzite. Hulin (2) reports beds of limestone in the Rand schist but none have been found near this deposit. The layering of the schist strikes generally northwest and dips southwest from 25° to 45°; this coincides with the original bedding. The large opencut (Fig. 5) explores a lenticular body of manganese minerals about 8 feet thick which lies parallel to the layering of the schist. Fortunately, the opencuts reveal the nature, relations, and distribution of the unweathered manganese minerals.

In the large opencut, the core of the lens, about 6 feet thick, is largely gray granular tephroite intimately mixed with gray granular manganese carbonate; the color and texture of the two minerals are so nearly alike that they can be

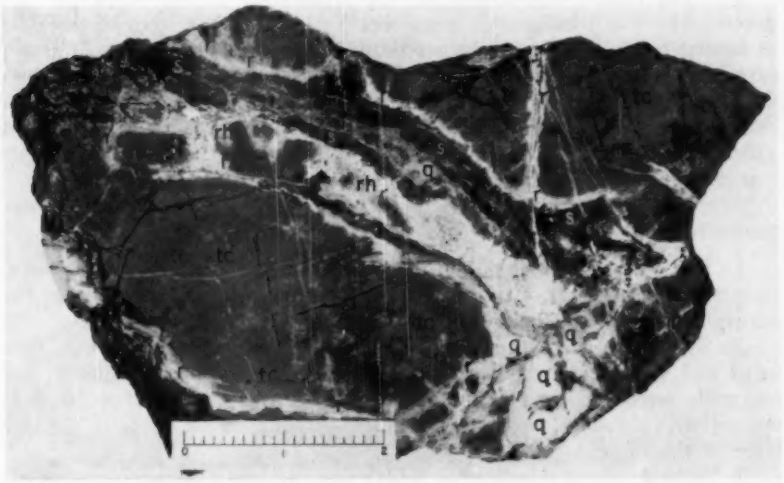

FIG. 6. Specimen from Big Indian mine, Kern County, Calif. Shows tephroite and manganese carbonate (tc) (medium gray), cut by veins of quartz (q) (white) and spessartite (s) (dark). Areas of tephroite-carbonate are surrounded by persistent zone of rhodonite (r) (light gray) partially altered to rhodochrosite (rh) (white).

distinguished only by etching with hydrofluoric acid or in thin section. In ten polished and numerous thin sections, the proportions of tephroite to carbonate range from about 9:1 to 3:1. In several large specimens, etched with hydrofluoric acid, the individual grains of tephroite show an elongation and lineation parallel to the layering of the schist and surrounding quartzite. The grains of quartz in the quartzite walls also show lineation and preferred orientation. Neither the walls nor core show veins of manganese minerals along which exotic manganese might have been brought into the lens; it appears that the manganese in the lens is indigenous. At the contact of the lens of manganese minerals with the quartzite, there is a narrow zone within which there is considerable magnetite, some garnet, potash feldspar, and

occasional flakes of stilpnomelane, the rare iron-manganese silicate—pyroxmangite, and riebeckite.

Most of the core of tephroite and carbonate is uniformly gray and equigranular, but in places there are zones of breccia cemented by veins that are largely quartz, spessartite, and rhodonite (Fig. 6). All of the fragments of tephroite-carbonate rock show a thin border zone of rhodonite crystals that have grown by replacing the tephroite-carbonate. Locally, the rhodonite is replaced by a thin layer of rhodochrosite. In some of the veins of rhodonite that extend outward into the tephroite-carbonate rock, there are thin veinlets of bementite. A few crystals of manganoan cummingtonite and anthophyllite were noted in the contact zone.

The Big Indian deposit presents the problem of the source of the manganese; (1) was it indigenous in sediments that formed the lens of carbonate as known in the Franciscan formation of the Coast Ranges, or (2) was it exotic, introduced after the sedimentary rocks of the Rand schist had been deposited? As the examination of this area has yielded no evidence of cross-cutting fractures or veins in the Rand schist adjacent to the lens of manganese minerals, it is considered that the manganese is indigenous in the lens, probably deposited as the carbonate in the sediments.

The paragenetic relations of the minerals of this deposit may be summarized as follows:

1. The oldest material of the lens is the tephroite-manganese-carbonate rock which forms most of the core. The relations of the grains of these two minerals are such that they seem to have crystallized simultaneously.
2. Somewhat later, the tephroite-manganese-carbonate rock was fractured and veins and irregular masses composed of spessartite, quartz, and magnetite were deposited in the fractures. Meanwhile, the silica (quartz) reacted with the host, tephroite-manganese-carbonate rock, to form the thin layer of rhodonite.
3. Probably about this time or a little later at lower temperature, a little water penetrated minor fractures and deposited the small veins of rhodonite and bementite.
4. The latest mineral deposited in the veins is rhodochrosite.
5. The quartzite shell that surrounds the tephroite-carbonate represents recrystallized chert. The formation of the spessartite, stilpnomelane, and riebeckite is due to the reaction between the various impurities that were contained in the original chert.

At the B.H.P. (Manganese Queen) prospects the principal exploration is an opencut about 75 feet long on a west-sloping hillside in the SE¼ sec. 36, T. 30 S., R. 40 E., Mount Diablo meridian, about 4 miles southwest of Randsburg (11). A shallow shaft lies 200 yards southwest, but it is no longer accessible. The area is underlain by the Rand schist in which the foliation trends northeast but local dips indicate open folds that plunge southwest. In the opencut, aggregates of manganese minerals form lenticular masses that are sporadically distributed in a bed of quartzite about 3 feet thick. Manganese garnet is the most abundant mineral in these aggregates; mostly

it forms persistent layers of minute crystals in a quartz matrix. A few lenses are largely rhodonite that forms reticulate masses of needle-shaped crystals, commonly with included minute crystals of garnet. There are a few lenses of dense pinkish manganiferous carbonate through which small garnets are distributed. In some lenses that are largely rhodonite, this mineral is replaced by plumose aggregates of pale-olive axinite, which is one of the late minerals of the assemblage. No tephroite was found in six thin sections examined.

The mode of origin of this deposit is not clear. Most of the lenses of manganese minerals lie parallel to the foliation of the schist. The internal distribution of the manganese minerals indicates that they represent manganiferous materials, carbonate, and possibly silicate, interlayered with siliceous sediments; the absence of cross-cutting veins that enter the manganiferous lens tends to confirm this mode of origin. On the other hand, however, at the upper (northern) end of the lens, the layering in the schist does not conform with the border of the quartzite lens. This unconformity may arise out of local movement when the rocks were deformed.

SUMMARY OF PARAGENETIC RELATIONS OF THE MINERALS AT DEPOSITS EXAMINED RECENTLY

Butte County: Bear Canyon mine.

1. Manganese carbonate, fine-grained, contains
   2. Tephroite in sporadic grains and aggregates surrounded, in part, by
      3. Rhodonite-spessartite aggregates and veins
         4. Bementite areas, sporadic
            5. Neotocite areas.

Nevada County: Manga-Chrome (Duggan) mine.

1. Manganese oxide (hausmannite) and manganese carbonate in layers, largely replaced by
   2. Tephroite, plumose aggregates, and veins cut by
      3. Rhodonite and spessartite in thin veins, also
         4. Bementite and barite in veins.

Nevada County: Smith prospect.

1. Manganese carbonate and oxide (hausmannite) layers, replaced by
   2. Tephroite veins with some bementite, followed by
      3. Rhodonite, largely on walls.

Amador County: Germolis prospect.

1. Manganese carbonate nodules, containing sporadic areas of grains of
   2. Tephroite, alleghanyite, surrounded by zone of
      3. Rhodonite with minor spessartite.

Mariposa County: Caldwell mine.

1. Manganese carbonate, oxide, and silicate layers, locally replaced by
   2. Tephroite, granular, and plumose aggregates in oxide and carbonate
      3. Rhodonite and piedmontite grains in silicate layers,
         4. Bementite in thin veins.

Kern County: Big Indian mine.

1. Manganese carbonate-tephroite rock, cut by veins of spessartite-quartz and replaced by
   2. Rhodonite, replaced by
      3. Rhodochrosite, and cut by
         4. Bementite veinlets.

Kern County: B.H.P. prospect.

1. Manganese carbonate lenses in Rand schist replaced(?) sporadically by
   2. Rhodonite, with spessartite, replaced by
      3. Axinite, plumose aggregates.

The evolution of the manganiferous materials in the sediments of the Calaveras formation and Amador group in the Sierra belt is summarized below.

The specimens recently collected and studied in polished and thin sections by the authors clearly represent sedimentary materials that have been largely recrystallized and locally rearranged. It is interpreted that the original sediments included (1) beds, lenses, or nodules of nearly pure carbonate of manganese, probably with minor amounts of iron, calcium, and magnesium; (2) beds of nearly pure manganese oxide; (3) beds of a hydrous silicate of manganese; and (4) beds of mixed carbonate and oxide of manganese, in part with small amounts of silica. The early work of Taliaferro and Hudson (4) recognized original beds of carbonate and silicate of manganese in stratigraphic sections largely made up of silica.

Tephroite is the earliest of the crystalline silicates of manganese and replaces both the original layered carbonate and oxide (now hausmannite). At each of the deposits, tephroite is very intimately mixed and intergrown with carbonate; at some deposits, tephroite replaces hausmannite. At two deposits, grains of alleghanyite are closely associated with the tephroite.

Distinctly following the formation of tephroite, rhodonite, with or without spessartite, was formed (1) as an outer layer or zone that envelops masses of carbonate and tephroite, or (2) as veinlets that cut these masses.

At several deposits, quartz, as veins or granular masses, follows the deposition of rhodonite and spessartite. Commonly, a little pyrite occurs with the rhodonite and with the quartz. Veins of granular barite also appear in this epoch.

Bementite appears in small amount as either feathery masses that replace the earlier manganese minerals or as narrow veins that cut across them. In places, barite appears in the bementite veins; neotocite locally replaces bementite and, in places, the terminal mineral is a carbonate.

SUMMARY

The present writers have examined recently only a few of the many manganese deposits in the Sierra Nevada belt, one in Butte County, two in Nevada County, one in Amador County, one in Mariposa County, and two in Kern County—seven in all. At four of these, Manga-Chrome and Smith

in Nevada County, Caldwell in Mariposa County, and Big Indian in Kern County, tephroite is present in abundance. At the two deposits in Nevada County and that in Mariposa County, tephroite is associated with abundant hausmannite, much of which appears to represent layers in the sedimentary section that were deposited originally as a different oxide. Also present in the sections were layers of manganese carbonate and silicate. In this environment, tephroite could form by the reaction of either the carbonate or oxide, or both, with silica or silicates.

In the other three deposits, in Butte, Amador, and Kern Counties, no hausmannite has been observed. Tephroite occurs intimately associated with manganese carbonate in an environment that contains abundant free silica. Even though the masses of manganese minerals show small veinlets of other minerals, there is no evidence in any of the six localities of major cross-cutting veins that would have permitted access of exotic manganese. It is concluded, therefore, that the silicate minerals, tephroite and rhodonite, were formed by static, thermal metamorphism, largely, if not wholly, in situ from local sources of manganese and silica. With reference to the manganese deposits in the Coast Ranges it has seemed advisable, however, to re-examine the large collections made by the authors and others in recent years. This re-examination confirms the record of earlier work, that tephroite is very rare in the deposits in the Franciscan formation of the Coast Ranges; in fact, thus far, the mineral has been definitely identified at only one deposit, that at Alum Rock Park, Santa Clara County.

The chemistry of the indicated paragenesis of the manganese minerals will be briefly summarized. Taliaferro and Hudson (4) state that the original minerals in the deposits of both the Sierra Nevada belt and the Coast Ranges, were probably syngenetic layers of manganese carbonates and amorphous silicates (manganese opal); recent work indicates that layers of manganese oxide, also, were present in the section of sedimentary rocks at several localities. The earliest effect of metamorphism, probably thermal through burial, was the development of the orthosilicate, tephroite, both in the layers and nodules of carbonate and in the layers of oxide and carbonate. As the MnO content of tephroite is 70.2 percent (sp. gr. 4.1), and of rhodochrosite, 61.7 percent (sp. gr. 3.7), it is clear that if replacement of manganese carbonate takes place without change of volume, some MnO must be added per cubic unit to form tephroite. If, however, layers of oxide are nearby, tephroite could form without the advent of exotic manganese. The general absence of major cross-cutting fractures near the large bodies of tephroite indicates that it has been formed largely by the combination of the carbonate or oxide with local silica or silicates.

Rhodonite, the metasilicate, contains 54.1 percent MnO (sp. gr. 3.7); bementite, the most common hydrous silicate, 40.2 percent MnO (sp. gr. 3.1); and neotocite, generally the latest silicate to form, from 20 to 40 percent MnO (sp. gr. 2.7–2.8). In the successive development of these minerals by the replacement of tephroite, therefore, there is a progressive loss of MnO per unit of volume and a corresponding increase in the local content of silica and water.

The record of previous work shows that a little pyrite, cinnabar, chalcocite, and metallic copper are widespread in the manganese deposits of the Coast Ranges; of these, earlier and recent work indicate that only a little pyrite is found in the deposits of the Sierra belt and this has formed during the deposition of rhodonite. The sulfides of mercury and copper with metallic copper indicate that exotic materials have been brought to the deposits in Franciscan rocks by exotic hydrothermal solutions.

Recent field work by the authors at several localities indicates that veins of axinite, a boron-bearing silicate, have been deposited late in the history of the deposits. Veinlets of axinite are the latest mineral at the Trout Creek deposit in Franciscan sedimentary rocks in Trinity County and on the Spider deposit in Triassic or earlier metamorphic rocks in Trinity County. Also, at the B.H.P. deposit in the schists of Precambrian age of Kern County, where the principal manganese minerals are rhodonite and spessartite, the latest mineral is veinlets of axinite. This boron-bearing silicate seems to indicate that the element boron was brought to the deposits by exotic hydrothermal solutions.

The work of the authors tends to confirm one of the conclusions of earlier workers that the minerals that are abundant in the Sierra belt deposits—the silicates, spessartite, piedmontite, rhodonite, as well as tephroite—indicate that the materials originally deposited in the sediments have undergone a higher degree of metamorphism than those of the Coast Ranges deposits where piedmontite is not known and rhodonite, spessartite, and tephroite are very rare.

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California Division of Mines, San Francisco and Los Angeles,
May 27, 1960

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LEAD ISOTOPES IN ORES AND ROCKS OF BUTTE, MONTANA

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ABSTRACT

The isotopic compositions of leads in ores and rocks of Butte, Montana, suggest that the ore metals were neither late stage concentrates from the crystallizing magma that produced the Boulder batholith, nor concentrates of trace metals from nearby sedimentary rocks. The ore metals probably were concentrated and isolated in several non-shallow locations about 400 m. y. ago and were then transported into the batholith by the late stage fluids of the magma, after the batholith was emplaced 60 m. y. ago. Mixing of host rock lead and ore mineral leads occurred in and near the ore zone.

INTRODUCTION

THE isotopic compositions of leads in some igneous minerals, sedimentary rocks, and sulfide ores of Butte, Montana, have been determined as a means of investigating the source of ore in the deposit. This paper is a report of preliminary results, and the scope of the data presented here is adequate only to make suggestions as to what may have occurred in this district. This is the first reported indication by isotopic data of a non-parental relation between hydrothermal ore and host igneous rock. The problem of explaining the significance of the data, despite their preliminary nature and because they contradict a majority viewpoint, requires a rather explicit presentation.

Variations in the isotopic compositions of leads within individual ore districts elsewhere have been described by Nier (9), Russell Farquahar, Cumming, Wilson, and Hawley (12, 13), and by Ecklemann and Kulp (6). Such variations are ascribed to mixing of common lead with radiogenic lead and give rise to J-type anomalous leads characterized by model ages younger than the emplacement age and large variations in isotopic compositions. In contrast, the isotopic compositions of the leads in the Butte district have model ages older than the emplacement age and exhibit small variations. The Butte leads fall into the catagory designated by B-type anomaly by Cahen et al. (2).

The Butte ores are considered classic examples of hydrothermal ore deposits (1). The mineralized area lies near the southwest margin of the Boulder batholith. The batholith is about 70 m. y. old (3), and is composed of granodioritic and quartz monzonitic rock types that cut sedimentary rocks Precambrian to Cretaceous in age. The quartz monzonite at Butte contains aplites and pegmatites, and is cut by quartz porphyry dikes. Subsequent events are Anaconda Age (East–West) mineralized fissures, Blue Age (Northwest) mineralized fissures and Northeast fissures with minor mineralization. Succeeding unmineralized fault fissures include the Steward, Rarus and Middle Systems, all northeasterly, and the Continental System (North–South). Post-mineral rhyolite dikes also cut the area.

The ore district exhibits a spatial zonation of mineral type. A Central zone, which enlarges at depth and contains chiefly copper minerals, is surrounded by the Intermediate Zone of copper, lead, and zinc minerals. The Outer zone is composed of lead and zinc minerals associated with manganese minerals (15, 11). Sales and Meyer (17) believe that the major structural epochs in which the principal fissures formed were not sharply defined but that there was an almost continuous process of structural readjustment of varying intensity throughout the tenure of ore deposition. The three mineralized fissure systems appear to represent three principal events in a structurally regulated, more or less continuous process of ore deposition in which the paragenesis and spatial distribution of minerals is approximately repeated. The quartz monzonite host rock is intensively sericitized close to the ore veins and argillized further outward (17).

SAMPLE DESCRIPTIONS

As an aid to sample identification, the East-West and Northwest fissure systems have been labelled I and II.

S-223: Galena from 400′ level of Lexington. Associated with sphalerite and silver minerals in the outer zone, fissure system I.

S-43: Galena from 1,000′ level of Emma Mine. Associated with sphalerite and pyrite in the outer zone, probably fissure system I.

S-60: Galena from 2,300′ level of Anselmo. Associated with sphalerite in the outer zone, fissure system I.

S-119: Galena from 3,200′ level of Anselmo. Associated with sphalerite and chalcopyrite in the outer zone, fissure system I.

S-118: Galena from 2,800′ level of Orphan Girl Mine. Associated with sphalerite, calcite, chalcopyrite, pyrite and quartz, in the outer zone, fissure system I.

S-175: Galena from 3,400′ level of Leonard. Associated with chalcocite and pyrite in the central zone, near Horsetail fissure system I.

S-97: Pyrite from 3,400′ level of Leonard Mine. Associated with digenite and pyrite in the central zone, near Horsetail fissure system I. Samples S-175 and S-97 were collected approximately 870 feet apart from North Bennett and East Colusa veins, respectively.

S-138: Pyrite from 4,200′ level of Mtn. Con. Mine. Associated with bornite and chalcopyrite in the intermediate zone, from an intersection of veins of fissure systems I and II. (May be from either.)

S-184: Pyrite from 4,200′ level of Mtn. Con. Mine. Associated with chalcopyrite in the intermediate zone, from an intersection of veins of fissure systems I and II. (May be from either.) Samples S-138 and S-184 are from nearby locations in two veins belonging to fissure systems I and II.

S-5: K-feldspar from a pegmatite cutting Butte quartz monzonite in a roadcut west of Nine Mile House southeast of Butte ore district. Both pegmatite and quartz monzonite are slightly altered or weathered, or both.

S-8: K-feldspar from a pegmatite on the northeast slope of Timber Butte, 600 ft. from the summit. The quartz monzonite here is cut by many small pegmatites and quartz veins.

S-1: Quartz monzonite one mile north of Walkerville in a rock quarry. This quartz monzonite is the least altered rock that was obtained close to the ore district. Potash feldspar and quartz were separated from the rock and analyzed individually.

S-4: Quartz monzonite from the same location as S-5 pegmatite. Potash feldspar and quartz were separated from the rock and analyzed individually.

Post-Precambrian Composite: A composite of fifteen samples of rocks from Cambrian to Lower Cretaceous age in the Camp Creek section. Each formation was represented by one sample weighted in proportion to the thickness of the rock type in the formation (14). In some cases, where several rock types were present in one formation, lead deficient types (such as quartzites) were not included.

Precambrian Composite: A composite of four samples of equal weight: one from Belt argillite, one from Belt limestone and two of Lower Precambrian schists and gneisses.

EXPERIMENTAL

Separation of the individual mineral phases from field samples was done as follows:

Galena.—Hand picked by an acid-cleaned stainless steel needle.

Pyrite.—Hand specimens containing largely pyrite and small amounts of chalcopyrite, bornite and chalcocite were crushed to $-80+120$ mesh in an acid-cleaned Diamond mortar and the individual mineral phases were separated in a cleaned Franz Isodynamic Separator. The pyrite fraction was treated three times with purified warm 3M HCl and washed repeatedly with quadruple-distilled water until no traces of acid were left.

Emission spectrographic analysis indicated that the pyrite fractions contained copper equivalent to 3 to 5 percent of chalcopyrite and chalcocite and the purity of the pyrite fraction was accordingly estimated to be about 95–97 percent.

Feldspars.—Small pieces of potash feldspars were hand picked from the pegmatite samples and ground in an acid-cleaned Diamond mortar, and the fraction $-80+120$ mesh was taken and acid cleaned as in the case of pyrite. Microscopic examination of grain mounted slides indicated the presence of only microcline and orthoclase.

Potash feldspar was separated from the $-80+120$ mesh fraction of the crushed quartz-monzonite. The light colored floats in tetrabromoethane were processed through a Franz Isodynamic Separator to remove any residual dark minerals. From this quartz-feldspar mixture, the density 2.57 floats were separated and retained. The potash feldspar concentrate was cleaned with 3M HCl as in the case of pyrite. Microscopic examination indicated a maximum of 3 percent impurities of plagioclase present as inclusions and small unseparated grains.

Quartz.—Quartz was separated from the $-50+100$ mesh fraction of the crushed quartz-monzonite. The dark and heavy minerals were separated out by heavy-liquids and magnetic separation. The density 2.65 floats, which were composed mostly of potash feldspar, plagioclase, and quartz were then treated in a solution of 48 percent Fluoboric acid with concentrated phosphoric acid and ferric chloride at 50° C for 48 hours as described in Hillebrand et al. (7). The fluoboric acid treatment was repeated until only quartz was left behind. The estimated purity of the quartz fraction was over 99.9 percent. The quartz was cleaned with HCl as in the case of pyrite.

Microgram quantities of lead and uranium were isolated and analyzed by some modification of the procedures given in Tilton et al. (19), and in Chow and McKinney (4). The isotopic compositions of leads in nine sulfide minerals are given in Table 1. In Table 2 are given the lead and uranium concentrations and the isotopic compositions of leads in some igneous minerals and sedimentary rocks. The error limits for the data in Tables 1 and 2 are those assigned by Chow and Patterson (5). These are ± 0.3 percent for the Pb^{206}/Pb^{204} ratio; ± 0.1 percent for the Pb^{206}/Pb^{207} ratio; and ± 0.2 percent for the Pb^{206}/Pb^{208} ratio. These limits cannot be used for interlaboratory comparison purposes. The absolute correc-

tions to raw lead data listed by Chow and Patterson were also used. Tentative error limits of ± 0.5 percent for the Pb^{206}/Pb^{207} ratio from our data can be used for interlaboratory comparison purposes. The amount of laboratory contamination lead introduced in the quartz lead samples was less than one part in a hundred, so that uncertainties in the amount and isotopic composition of contamination lead were negligible in determining the concentration and isotopic composition of the quartz lead.

DISCUSSION

We have arbitrarily chosen 60 m. y. as the age of ore mineralization in the Boulder batholith because the 70 m. y. figure obtained by Chapman et al. tends to an upper limit. The date refers to the early mineralization of the host rock, and the Larson age method used by them is maximal because of the lack of correction for original lead in the zircon. We have used 60 m. y. for the radiogenic correction in the Butte rocks since the time of ore mineralization, but the significant conclusions of this paper are not affected by a choice of either 60 or 70 m. y. in the computation.

The lead compositions of the samples at the time of ore mineralization 60 m. y. ago are plotted in Figure 1 to show the variation of Pb^{206} relative to Pb^{207} and Pb^{204}.[1] The lead in the Butte ore minerals is anomalous. From observed oceanic and ore lead data, it is believed that we know what most of the lead in the earth's upper crust was like 60 m. y. ago, and if the leads in the ore minerals of Butte are compared with such lead, they are deficient in Pb^{206}. If it is assumed that the isotopic composition of primordial lead in the earth was uniform everywhere, we are forced to conclude that the Butte lead was derived from a chemical system that was grossly depleted in uranium at a time much greater than 60 m. y. ago. This characteristic has been labelled a "B-type anomaly" by investigators at the University of Bern. According to this view, three events are postulated to have occurred in succession: first, a gross differentiation between uranium and lead during a short interval; second, a long period of isolation of the lead-rich, uranium-poor differentiate; and third, a final mobilization of the lead-rich differentiate into a new ore zone. The time of the first differentiation of the ore metals now found in the Butte area was about 400 m. y. ago, if the event was catastrophic. This is illustrated in Figure 1, where the 400 m. y. primary isochron is shown to pass through the cluster of ore mineral leads. The assignment of a 400 m. y. isochron age to the Butte ore lead is simply an abbreviated way of postulating that, starting 4,550 m. y. ago, the lead evolved normally from iron meteorite lead for a period of 4,150 m. y. in a system where the U^{238}/Pb^{204} ratio today is equal to 9. The trend of evolutionary growth is given by the line A in Figure 1. The lead stopped evolving 400 m. y. ago instead of continuing to evolve until 60 m. y. ago; hence the lead appears anomalous relative to 60 m. y. old leads.

[1] This presentation is an unfamiliar variation of the commonly used Pb^{206}/Pb^{204} *vs.* Pb^{207}/Pb^{204} plot, and we use it advisedly. In order to properly utilize mass spectrometric measurement data in a graphical presentation of common lead data it is a necessary requirement and we urge its acceptance. The percentage error of a Pb^{206}/Pb^{207} coordinate is less than half the percentage error of a Pb^{207}/Pb^{204} coordinate. The gross aspects of the Pb^{206}/Pb^{204} *vs.* Pb^{207}/Pb^{204} plot are unchanged for the time span involved.

Although the lead in the ore minerals is anomalous, the lead in the igneous host rock is not. It is believed that a large part of the lead in rocks of this type is contained in the potash feldspars, and we investigated the lead not only in the feldspars of two different samples of the quartz monzonite, but in two different pegmatites as well. All of these samples originated from or near the ore zone,[2] and all of the feldspar minerals contained significant amounts of a dusty, opaque material that we believe is an alteration product of the feldspar. We believe that both the alteration around the aplite-peg-

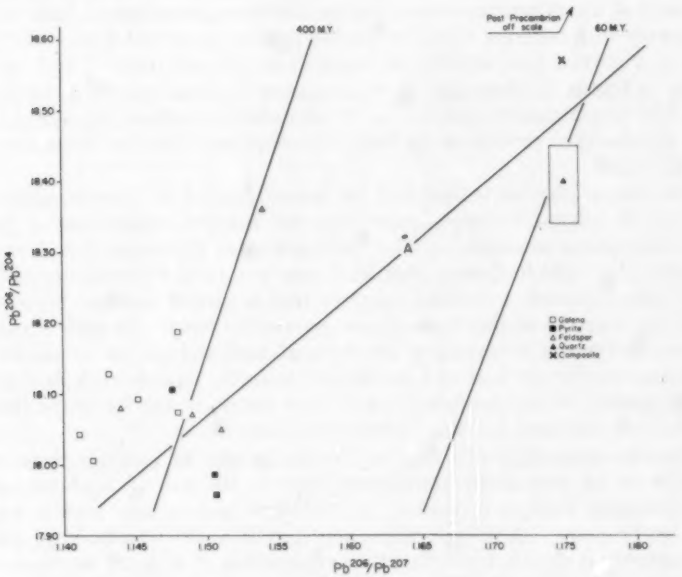

FIG. 1. The isotopic composition of the Butte, Montana, leads at the time of ore mineralization 60 m. y. ago. The measurement error limits for each point are illustrated by the block around the quartz lead. The line A represents a primary growth curve ($\mu = 9.0$, $T_0 = 4.55 \times 10^9$ years, $Pb_{primordial}$ = that in iron meteorites). The other two lines are primary isochrons.

matites in Boulder batholith rocks described by Neuerberg (8) and the hydrothermal alteration in the Butte area are primarily caused by late stage fluids of magmatic differentiation. In the case of Butte, these fluids were also the mobilizing agents and carriers of base metals that had already been isolated at an earlier time. In as much as the rock feldspars at Butte have been exposed to the pervasive influence of these late stage fluids, it is quite

[2] We use the term "ore zone" in a geochemical sense. In this sense, the limits of the ore zone are not determined by economic possibilities. Consequently we prefer to say that all of the feldspar samples originated from or near the "ore zone," although the samples are from rocks located from 1 to 7 miles from the mining district.

likely that lead in the feldspars has been contaminated. Therefore, we investigated the lead in a quartz mineral separate from the least altered sample of quartz monzonite and considered this lead to be most representative of that in the igneous rock. Quartz is comparatively resistant to hydrothermal alteration (18) and may have remained a closed system with respect to trace impurities since its first crystallization in the igneous host rock.

It is most likely that lead in batholithic rocks will be a normal lead if the batholith materials were derived from a lower crustal source. One could also expect that in the event of batholith formation by melting of large amounts of a sedimentary rock complex, the homogenization of leads in these sediments with different Pb/U ratios will produce a normal lead. The quartz lead is a normal lead, entirely different from the ore mineral lead, as illustrated in Figure 1, where the 60 m. y. primary isochron is shown to pass near it. The single quartz analysis is not considered spurious since it fits well into the observed pattern of the isotopic evolution of lead for large masses of crustal rocks.

In view of this, we believe that the normal lead of S-1 quartz, rather than that in the altered feldspars, represents the isotopic composition of lead in the Butte quartz monzonite. The investigation of Patterson, Silver and McKinney (10) which showed that lead was isotopically homogeneous in the Southern California batholith, suggests that a similar isotopic homogeneity could be expected in the Butte quartz monzonite body. In such a case, the isotopic difference between the ore mineral lead and quartz monzonite lead indicates that the ore lead was not derived from the igneous rock by a process of differentiation and concentration of base metals in the late-stage fluids as commonly postulated for this hydrothermal deposit.

The questionability of using lead isochron ages in geologic chronometry should not be mistakenly transferred here to the use of isochron ages in characterizing isotopic evolution. A Paleozoic galena may give a negative lead isochron age. Although this is very bad from the standpoint of geologic chronometry it does not mean that an explanation of why the isochron age is negative is equally bad. The isotopic data reported here contradict the majority view regarding the origin of the Butte ores. The weight of the isotopic arguments rests upon the plausibility of applying the gross features of the lead evolutionary model to the rocks in the Butte area. We believe the available isotopic evidence constitutes a valid and serious argument against the suggestion that the ores were derived by differentiation and concentration in the late-stage fluids of a magma.

There is no evidence that sedimentary rocks near the Butte area contain lead similar to the lead in the ore minerals. It can be expected that variations of the Pb/U ratio in sedimentary rocks will create, in time, an isotopic heterogeneity of lead in them. We made a composite of samples from the Post-Precambrian sedimentary rocks of the Camp Creek section near the Butte area. The rock type in each formation was represented by one sample weighted in proportion to the thickness of the rock type in the formation. Approximately 70 percent of the section was represented. Lead from this

composite of sedimentary rocks is anomalous, and contains an excess of Pb^{206}, as shown in Figure 1. The cause of this anomaly may be due to the highly abnormal μ observed in these rocks, which is about 30, compared to the normal U^{238}/Pb^{204} ratio of about 10. Lead from a composite of four sedimentary and metasedimentary rocks situated below the Cambrian-Precambrian unconformity is normal, as shown in Figure 1. The normal μ observed in these latter rocks may account for the normal isotopic character of the lead in them despite their great geological age and sedimentary origin. The isotopic differences that exist between leads in the now exposed sedimentary and metasedimentary rocks on the one hand and leads in the ore

TABLE 1

ISOTOPIC COMPOSITIONS OF LEADS IN SULFIDE MINERALS FROM THE BUTTE, MONTANA AREA

Sample	206/204	206/207	206/208
S-223 Galena	18.04	1.141	0.463
S-43 Galena	18.13	1.143	0.462
S-60 Galena	18.07	1.148	0.464
S-119 Galena	18.19	1.148	0.463
S-118 Galena	18.01	1.142	0.462
S-175 Galena	18.09	1.145	0.463
S-97 Pyrite	18.11	1.148	0.465
S-138 Pyrite	17.99	1.151	0.467
S-184 Pyrite	17.96	1.151	0.466

minerals on the other indicate that the ore metals probably were not mobilized from locations within upper sections of adjacent sedimentary rocks.

The isotopic compositions of leads in the ore minerals and the feldspars show a heterogeneity which may be the result of mixing of leads of different compositions. The lead in the feldspar from the least altered sample of the host rock has an isotopic composition intermediate between the galena leads and the quartz lead, and lead in the feldspars from the most altered pegmatites and host rock is similar to ore leads. However, the deviation of the various leads from a two component mixing model is so large relative to our measurement error that it is doubtful that they are simply different mixtures of one kind of ore lead and one kind of rock lead. There is a strong indication of multiple component mixing and a consequent implication

TABLE 2

ISOTOPIC COMPOSITIONS OF LEADS AND THE CONCENTRATION OF LEAD AND URANIUM IN SOME IGNEOUS MINERALS AND SEDIMENTARY ROCKS OF THE BUTTE AREA

Sample	Pb content, ppm	U content, ppm	Pb^{206}/Pb^{204}	Pb^{206}/Pb^{207}	Pb^{208}/Pb^{206}
S-5 Pegmatite K-feldspar	53	0.47	18.08 18.07*	1.149 1.149*	0.466
S-8 Pegmatite K-feldspar	—	—	18.08	1.144	0.467
S-1 Qz-monzonite K-feldspar	45	0.36	18.36 18.36*	1.154 1.154*	0.466
S-4 Qz-monzonite K-feldspar	—	—	18.05	1.151	0.467
S-1 Qz-monzonite quartz	0.20	0.027	18.48 18.40*	1.180 1.175*	0.464
S-4 Qz-monzonite quartz	0.13	0.025	—	—	—
Post-Precambrian composite	9.0	3.7	19.92 19.67*	1.245 1.230*	0.500
Precambrian composite	9.3	1.5	18.67 18.57*	1.181 1.175*	0.478

* Isotopic composition corrected for the addition of radiogenic lead in the last 60 m. y.

of a multiplicity of ore sources. The composition of an ore mineral lead does not appear to be determined by its position in the district zoning pattern. Further studies are planned to explore in greater detail some of the tentative conclusions arrived at in this paper.

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SULFIDE ORES FORMED FROM SULFIDE-DEFICIENT SOLUTIONS[1]

T. S. LOVERING

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ABSTRACT

Assuming that many hydrothermal ore deposits are formed from emanations given off from a magma at depth while it cools through the interval in which latent heat of crystallization is generated, it is shown that this cooling interval for magmatic bodies of moderate size must be measured in tens or hundreds of thousands of years.

Emanations from such a magma should change at the source with time: relatively insoluble volatiles should depart early and the more soluble ones late; the general order is probably sulfur gases and oxides of carbon, water, chlorides, and fluorides. Experimental and field evidence indicates that this order approximates the increasing solubility of these gases in natural magmas.

Theoretical considerations show that within a hydrothermal conduit a relatively small gradient would soon be established between the magma and the surface. A small gradient suggests that temperature drop is a minor factor in precipitating substances in solution, whereas a drop in pressure and reaction with wall rocks or with material precipitated from earlier emanations would be of major importance. The sulfur-rich early

[1] Publication authorized by the Director, U. S. Geological Survey.

emanations tend to react with indigenous iron of the country rock, or with iron carried by carbon dioxide-rich solutions to where a marked pressure drop occurs; either of these reactions will form abundant early iron sulfide. Later sulfur-deficient emanations, which then carry soluble halides of ore metals, react with this early iron sulfide to precipitate the ore mineral sulfides by replacement and deposition with loss of iron to the solution. Precipitation of much sulfide ore is thus commonly accomplished by sulfur that was fixed near the site of the ore body by earlier emanations from the magmatic source; a large amount of ore, however, may be precipitated from late-stage magmatic solutions where they mingle with early-stage sulfur-bearing solutions from a different magmatic source.

INTRODUCTION

In this paper evidence is given for the following conclusions: (1) magmatic emanations that leave the magma during its consolidation may move out of it for a long period of time; (2) magmatic emanations normally change in character at their source with time; (3) sulfur is abundant at an early stage whereas halogens become abundant later; (4) the emanations will change enroute to the surface by reaction with country rock or with material deposited or precipitated from an earlier stage emanation, or by mingling with emanations from a different magmatic source, or with ground water. Some of the probable consequences of these conclusions suggest a different interpretation of ore genesis from that commonly accepted, but I am not writing a critique of current theories of ore deposition.

Necessarily the discussion is limited here to sulfide deposits of magmatic affiliation—those that are generally encompassed in the terms magmatic hydrothermal or pneumatolytic sulfide ores. The evidence suggests that many such ores are deposited from solutions essentially free of sulfides through the reaction of alkaline, neutral, or acid metal-bearing solutions with previously deposited iron sulfides or by reaction with sulfur-bearing gases from a different source. Before these chemical processes can be properly considered, however, certain aspects of the cooling of the igneous bodies from which the volatiles escape must be appraised, especially those that affect the time, temperature, and the manner of their release.

TIME INTERVAL FOR DEPARTURE OF VOLATILES FROM MAGMA

Theory.—It is assumed that the ores are products of emanations from a silicic or intermediate igneous magma intruded as a discrete mass some 2 to 10 km—or even more—below the surface, although the ores themselves may precipitate at depths of much less, perhaps 1 to 4 km from the surface. The magma is presumed to contain 1 to 5 percent water by weight, and ore elements, sulfur, carbon, and halogens amounting to a few tenths of a percent in toto. Most of the volatile components normally will be given off during the period of crystallization of the anhydrous and hydrous rock silicates—the stage during which latent heat of crystallization is evolved. A reasonable figure for the solidification *interval* of the magma is 100 to 300° C, and Larsen (21) has used an interval of 200° for the Sierra Nevada batholith,

which he assumes is intruded at a temperature of 700° above that of the country rock. His calculations, however, do not properly consider the effect of latent heat of fusion, because of the mathematical difficulties involved. Price and Slack (33) and more recently Jaeger (17) have devised better methods for evaluating the effect of latent heat for heat-flow equations and Jaeger has applied this technique to the solution of some special geological problems.

One of the striking results of this work is the evidence that the length of time required for crystallization and cooling of a sheet increases enormously as the temperature difference between the country rock and the intrusive diminishes. Some idea of this relationship can be had from the equation for the position X of the plane at which solidification of a semi-infinite liquid mass is just completed, which is given by equation 1.

$$X_s = 2\lambda(\kappa_1 t)^{\frac{1}{2}} \tag{1}$$

where X_s is the distance from the original plane of contact, κ_1 is the diffusivity of the solidified magma, t is time, and λ is a numerical parameter which is the root of the transcendental equation:

$$\frac{1 - \operatorname{erf} b\lambda}{1 + \operatorname{erf} \lambda} \exp[(b^2 - 1)\lambda^2] = \frac{a(T_2 - T_1)}{T_1}$$

where T_2 is the temperature of intrusion, T_1 is the temperature of solidification,

$$a = \frac{K_2\kappa_1^{\frac{1}{2}}}{K_1\kappa_2^{\frac{1}{2}}}; \qquad b = \left(\frac{\kappa_1}{\kappa_2}\right)^{\frac{1}{2}},$$

K_1 is the thermal conductivity and κ_1 the thermal diffusivity of the solidified magma (the thermal properties of which are identical with those of the country rock), K_2 is the thermal conductivity and κ_2 is the thermal diffusivity of the liquid magma, and finally the error function or "probability integral" erf of λ is:

$$\operatorname{erf} \lambda = \frac{2}{\pi^{\frac{1}{2}}} \int_0^{\lambda} e^{-\beta^2} d\beta$$

for which tabulated values are available. Jaeger has calculated the values of λ for a wide range of solidification intervals and for values of $L = 100$ and $L = 80$, where L is the latent heat of crystallization in calories per gram.

The rate at which the plane of solidification moves forward (until the temperature in the center commences to fall) is

$$\frac{X_s}{t^{\frac{1}{2}}} = \lambda(4\kappa_1)^{\frac{1}{2}}. \tag{2}$$

From this it follows that where the plane separating the completely solid rock from the melt is the same distance from the contact in two bodies with identical thermal constants, one body intruded at a different temperature or with a different melting interval than the second, the relationship of the time intervals

required for the plane of solidification in the two different bodies to reach this place can be expressed as follows:

$$t_2 = t_1 \left[\frac{\lambda_1}{\lambda_2}\right]^2. \qquad (3)$$

Where t_1 is the time interval of solidification to the point X_s for which λ_1 is appropriate and t_2 is the similar time interval for the material for which λ_2 applies. It thus appears that the time for solidification where latent heat of fusion is evolved varies as the square of the ratio of the parameter λ during the early stages of consolidation. An idea of the effect of the melting range and the initial difference in temperature between the country rock and the melt is obtained by inspecting the values of λ given in Jaeger's Table 1 (17, page 309). A few selected values of λ taken from Jaeger are given below.

TABLE 1

VALUES OF λ

Temperature difference between magma and walls	Melting range	L = 100		L = 80	
		Tct	λ	Tct	λ
1,400–1,300	100	833	0.55	812	0.59
1,400–1,200	200	832	.41	812	.45
1,400–900	500	818	.090	803	.11
1,200–1,100	100	728	.49	708	.54
1,200–1,000	200	726	.35	707	.38
1,000–900	100	621	.42	603	.47
1,000–800	200	617	.27	600	.30
1,000–700	300	609	.13	595	.16
1,000–600	400	597	.004	586	.022
800–700	100	512	.34	496	.382
800–600	200	504	.17	490	.201
800–500	300	491	.016	480	.036
700–500	200	446	.11	434	.14
600–500	100	398	.23	386	.269
600–400	200	385	.036	375	.060
400–300	100	276	.076	268	.106

L = Latent heat of fusion.
Tct—Temperature at contact.
λ defined on page 70.

Jaeger's work thus indicates that the initial rate of advance of the plane of solidification in a magma having a crystallization range of 100° and intruded at a temperature 1,200° above its surroundings, would be nearly 50 times as rapid as for the same magma intruded into country rock that was only 400° cooler than the magma, and about twice as rapid as the cooling of the same magma injected into wall rocks that were 800° below the temperature of the intrusion.

The specific geologic problems solved by Jaeger include those of the temperature distribution in an intrusive sheet in an infinite medium and in a sheet intruded under half its thickness of cover. Using constants appropriate

for diabase and assuming an initial temperature above the wall rock of $T_0 =$ 1,000° C, and a temperature of solidification $T_s = 800°$, Jaeger shows that only a very small difference is to be expected for the time intervals required for solidification of the sheet under deep cover and for the one under a cover equal to only half its thickness.

Under the conditions assumed for the intrusion and the generation of latent heat ($L = 100$), Jaeger's solution shows that the time in years for complete solidification is equal to $0.016 \times d^2$, where d is the diameter in meters, or for a sheet 5 km thick, $0.016\ (5{,}000)^2$ or 400,000 years. Even for a sheet measuring only 2 km in diameter, the time of consolidation would amount to 64,000 years. It would seem then that the consolidation of a body of igneous rock large enough to supply emanations in quantities sufficient to form major ore districts must of necessity involve a span of time measured in tens or hundreds of thousands of years.

Jaeger's solution for a sill intruded under half its thickness of cover shows that its temperature gradient from the surface to the igneous body will plot as a straight line corresponding to the difference between the temperature at the contact of the intrusion with the country rock—which is only some 10 or 20° below the initial contact temperature—and the surface temperature, by the time $0.002\ d^2$ years have passed (where d is the thickness of the sill in meters), and that thereafter the temperature at the contact will fall very slowly until the time when consolidation is first complete. At that time the temperature in the center would be 200° less than the initial temperature and the temperature of the upper contact would have dropped approximately 150° C below its first value, from 617° to about 465° C, but the temperature of the lower contact would have fallen less than 20° C to about 600° C.

I have shown experimentally, and it can be demonstrated mathematically, that end effects for a rock body whose diameter is 5 times its thickness are negligible in the central part of the sheet. If we then use Jaeger's solution and assume a body 5 km in thickness, 25 km in its major diameter, intruded at a depth of 6 km, in a region where the average surface temperature is 20° C and the temperature gradient is 30° per km, the temperature at the depth of intrusion would be 200° C. Let us assume that the magma was intruded at a temperature of 900° and that its solidification range is 200°; this would mean that its initial temperature was 700° above that of the country rock, and that it solidified at an average temperature about 500° above that of the country rock. These temperature conditions correspond to one of the problems solved by Jaeger and illustrated by his Figure 1, which also applies to the condition specified by Larsen for the Sierra Nevada batholith. The thermal constants are those appropriate to quartz monzonite or quartz diorite: $L = 80$, $k = 0.005$; $c =$ specific heat $= 0.28$.

Data for the problem solved by Jaeger suggest that the temperature gradient from the upper contact of the intrusion we are considering, where the temperature of the intrusion is only 700° C above that of the country rock as contrasted with the 1,000° assumed by Jaeger, will adjust to an initial contact temperature of 634° C, e.g., 434° + 200°. The temperature of the lower contact will slowly fall to approximately 625° at the time when the

consolidation of the magma is complete, and that of the upper contact under 6 km of cover would not be much less—approximately 600° C. If ore deposition commenced 3 km below the surface, e.g., half way between the top of the magma and the surface, the initial temperature of the wall rock at this point would be 110° C. The temperature of the country rock here (3 km below the surface) would soon rise to about 330° and remain at essentially the same temperature until the central part of the intrusion was crystallized and the magmatic emanations had ceased as such. The heat contributed by the emanations to the country rock would raise temperatures of the conduit walls, the actual amount of heat contributed would depend on composition, pressure, volume, and velocity of the fluid passing through the conduit, the temperature of the country rock and of course the temperature of the emanation. The temperature gradient in the rock above the intrusion after initial solidification would probably give rise to hot-spring activity in areas of deep ground water circulation for a long period after the magmatic emanations had themselves ceased. These problems are discussed in detail on later pages.

Experimental Work.—It is possible to investigate the thermal behavior of bodies by the use of thermal models of small size where the materials of the model and the prototype are identical, and if latent heat of fusion is involved, the temperature differences between the model and its surroundings must be identical with that of the prototype and its surroundings. Although the writer has not investigated rock materials as yet, it is possible to discover certain characteristics from the investigation of low melting materials that have significance in appraising the shape factor for geologic materials. Using wax models (m.p. 50° C) under conditions where the contact temperatures approximated 70 percent of the initial difference in the temperature of the liquid and that of the surrounding material, it was discovered that the shape factors for a rectangular parallelepiped are essentially the same as those deduced—and measured—for the similar shaped material where latent heat of fusion was lacking. If the central part of a face of the parallelepiped had an initial contact temperature of 0.7 T_0, where T_0 is the initial temperature of the mass, then the edge where two faces joined had a contact temperature of $(0.7)^2\ T_0$, and the corners where three faces joined had an initial temperature of $(0.7)^3\ T_0$—temperatures that remained almost constant until the center of the parallelepiped solidified. When the wax model was introduced into material at either higher or lower temperatures than that obtaining in the foregoing illustration, the contact temperatures—as percentages of the initial temperature—fell or increased appreciably as would be expected from the mathematical analyses made by Jaeger.

If we apply the experimental results to the concept of a solidifying magma in a shallow hearth, it is obvious that we must modify our estimate of the thermal gradient suggested in the discussion of Jaeger's results given above. If we picture the roof of a batholith as corresponding to one edge of a rectangular parallelepiped the temperatures above the roof would be substantially less than those above a flat sheet, and over a cupola or the apex of a rudely pyramidal stock conditions similar to those at the corner of the rectangular

parallelepiped would be expected. Along the roof ridge of a batholith equivalent to that considered later, the contact temperature would be equivalent to $700° \times (0.63)^2 + 200° = 469°$, and the temperature half way to the surface would be $20° + 469 - 20/2 = 245°$ during most of that part of the thermal history of the batholith characterized by magmatic emanations. Immediately above the apex of a pyramidal stock, however, the initial contact temperature of the country rock with the apex would be only $700° \times (0.62)^3 + 200° = 367°$, and the country rock at 3 km would be 193° C, a temperature not unreasonable for the environment of hydrothermal sulfide ores.

Field Evidence.—The evidence for the length of time that fumaroles and geysers now active have been in existence is surprisingly scanty. Arnold Hague (14) showed that the thermal waters and steam vents of the Yellowstone National Park in the United States were in existence before the last glacial advance. Recent work by G. M. Richmond of the U. S. Geological Survey (oral communication, March 11, 1960) has shown that the Madison Plateau rhyolites, which surround the Upper, Lower, and Norris Geyser Basins, are earlier than Pinedale (Wisconsin) glaciation and later than Bull Lake (Iowan ?) glaciation; these lavas are locally altered by hot spring activity but in much less degree than older lavas. Gravels of Pinedale age that overlie the older lavas in the vicinity of active hot springs are much altered, but not as strongly as the older lavas themselves. The latter are completely argillized to a depth of more than 15 feet, suggesting that they may have been attacked well before the Pinedale gravels were laid down. Richmond concludes that the present system of geysers have been active at least since the close of Pinedale glaciation, and probably since the eruption of the post-Bull Lake-pre-Pinedale rhyolites—or about 30,000 years. He also suggests that other geyser systems probably existed in the area prior to the extrusion of these rhyolites.

D. F. White (oral communication) has observed thermally altered boulders in the glacial material of the lower Geyser Basin in the Park, boulders that show argillic alteration characteristic of acid hot springs at the surface. This evidence and the presence of hydrothermally altered rocks at the surface showing the characteristics of deep alteration lead White to believe that hot springs and geysers have been active in this area for at least 50,000 years. After a detailed study of the Steamboat Springs area in Nevada, White (41, p. 1642; p. 110) gives as his best estimate something between 100,000 and 1,000,000 years for the time during which the geysers and thermal waters have been active in that area.

Barth (4) and other students of the volcanic fields of Iceland believe that modern vulcanism began approximately a million years ago and has continued uninterruptedly through Pleistocene and Recent times. According to Barth, the type spouting hot spring called Geysir—from which our term geyser has come—has been carefully studied by Thorarinsson who concluded that the stratigraphy and structure show that the thermal activity in this area is approximately 10,000 years old and has lasted through all post-glacial time. Observations at the "Washing Springs" 3 km east of Reykjavik, which were discovered in the 9th century by Ingold Arnason, show that its

present temperature of 89° has fluctuated by only a fraction of a degree since 1772 when the first measurements were made. Such meager evidence as is available from Iceland suggests that the thermal activity as evidenced by geysers should be measured in tens of thousands of years rather than in smaller intervals of time.

The data from the well-known geyser fields of New Zealand is even more scanty and one can say only that geologic studies indicate almost continuous activity from the Miocene to the present and that there is little change in the general appearance of the geysers and geyser deposits from that described by the earliest explorers nearly a hundred years ago.

Less direct but suggestive evidence is furnished by the relations of ore deposits themselves to various intrusives. Although there are innumerable examples to be found in ore deposits scattered throughout the world, it will suffice to point out some of the relations in the Mineral Belt of Colorado, U.S.A., with which I am especially familiar. This mineral belt extends northeasterly for 250 miles from the La Plata Mountains to the eastern edge of the Front Range not far north of Boulder, Colorado. The belt crosses major northerly-trending Laramide structures without change in trend but is itself of Laramide age (Late Cretaceous and Paleocene), and is marked throughout its course by a wide variety of porphyritic intrusive rocks ranging in form from dikes and stocks to small batholiths. The igneous activity and the genetically related ore deposits are broadly contemporaneous and are not earlier than Paleocene nor later than early Eocene, but the individual districts show age differences in the ores themselves and in the porphyritic intrusions. There are many local centers of mineralization, and the hydrothermal solutions emanating from the local magmatic sources at corresponding periods in their magmatic history deposited ores that show a similar sequence of mineralization, although characterized by a different abundance of the individual minerals. In some of the districts, early base metal ores which are apparently related to quartz-monzonite porphyry magmas are cut by bostonite porphyry, and both are cut by pyritic gold ores which in turn are earlier than biotite latite and its associated telluride ores (26, p. 45, 84, et seq.). Within the base metal veins that are related to the quartz-monzonite porphyries, there is ample evidence of early hydrothermal alteration, deposition of ores, accompanied by intramineralization faulting, and late deposition of gangue and ore minerals such as is common in so many ore deposits. Although no definite time interval can be ascribed to such relations, the evidence seems clear that magmatic emanations moved outward along the pre-mineral fault channels for a very appreciable length of time.

Conclusions as to Time Interval During Which Volatiles Depart from the Magma.—Although only a small amount of the evidence available is summarized above, it seems sufficient to demonstrate that the time interval during which magmatic emanations are given off from a consolidating magma of sufficient size to generate appreciable ore deposits must be measured in tens or hundreds of thousands of years. It is also evident that the major part of the magmatic emanations could leave the magma while a nearly constant temperature gradient existed in the rock between it and the surface of the

earth, except where modified near hydrothermal conduits by heat exported in emanations, and that the general gradient elsewhere would change little during the departure interval.

CHANGE IN COMPOSITION OF MAGMATIC EMANATIONS AT SOURCE

Theoretical Considerations.—The departure of fugitive constituents from a highly complex chemical system, such as a magma, is not amenable to exact thermodynamic calculations. The laws for ideal solutions are obviously inapplicable excepting as the most general of guides. Numerous excellent phase studies have been made of pertinent silicate systems, but these have dealt mostly with anhydrous melts. In recent years there has been increased interest in the structure and thermodynamic analysis of silicate melt systems in equilibrium with volatile components, but we are a long way yet from a rigorous treatment of the problem.

The distribution law for a solute in two immiscible solvents is:

$$\frac{C_1}{C_2} = k \qquad (4)$$

and has interesting implications in the hydrothermal differentiation of material from a consolidating magma. Neumann (30) treats the problem mathematically using the following assumptions:

1. A hydrothermal solution separates as an independent phase (here called the "fluid phase"), in equilibrium with a molten silicate magma (called the melt) and its solid phases.
2. Constituents of the magma not entering the solid phase may be present in different concentrations in the fluid phase and the melt.
3. Either: a. the fluid phase is removed as fast as it is formed:
   or: b. the fluid phase remains in equilibrium with the silicate melt until it is completely crystallized.

The problem is essentially that of devising a mathematical expression relating the change in concentration of a soluble constituent of the two fluid phases as a function of: (a) its distribution coefficient for the immiscible fluid and the melt, and (b) as a function of the percent of the melt that has crystallized. The mathematical analysis of both conditions, i.e., whether the fluid phase remains in equilibrium throughout the freezing of the magma or whether it is given off from the melt as rapidly as the new phase forms, leads Neumann to make the following generalizations: where the ratio of the solubility of a compound in the magma to the solubility in the fluid phase is k, the concentration of the compound appearing in the fluid phase will be the same from first to last if the total amount remaining in the magma is the same as the total amount entering the fluid phase, i.e., where k is identical with the solubility of water in the magma, assuming that water is the major constituent of the coexisting fluid phase. If k is less than the solubility of water in the magma, i.e., if the solubility of the compound in water is more than the solubility of water in the magma, the compound will be enriched in the earliest hydrothermal solutions, as more of the compound will enter the fluid phase

at an early stage before much of it has been extracted from the magma. Conversely, a compound will be enriched in the late hydrothermal solutions if k is greater than the solubility of water in magmas, as for this condition the concentration of the compound in question will increase in the molten magma as crystallization proceeds and the quantity of molten phase diminishes. These generalizations merely restate the assumption that the distribution coefficient remains constant regardless of the concentration of a compound present, and that if the compound is removed from the system by the removal of one phase, the subsequent extractions will reflect this difference. Or if the concentration is changed by reducing the total quantity of one phase—as by crystallization—extraction of the compound from this phase by the fluid will reflect the increased concentration in the liquid remaining.

In addition to the discussion presented by Neumann, the implications of Henry's law [2] as to the manner of departure of volatiles from a magma is of importance. This is a special case of the general relation that the vapor pressure of a volatile in a liquid at a given temperature is a function of the concentration of the volatile in the liquid. Where this function is known for a given temperature, the solubility of a gas at some new pressure, or the vapor pressure of a solute at some new concentration, can be calculated. There are wide deviations from Henry's law for many gases but others show a close correspondence between theory and experiment; in general, the higher the temperature the better is the agreement. It is perhaps better to regard the relationship expressed by Henry's law as a special case of the expression $C = f(p)$, where $f(p) = k'p$, and

$$C = k'p \tag{5}$$

where $k' = 1/k$. Experimental data suggest that commonly $f(p) = mp^n$, and therefore a more general statement of the relation of pressure to concentration is:

$$C = mp^n \tag{6.0}$$

where m and n are constants determined by experiment. Equation 6.0 makes it possible to calculate the volume of gas lost from a solution at constant temperature as the pressure decreases from any assumed initial vapor pressure. For some studies it is advantageous to use the general form of 6.0 but to change the expression to $p = f'(p)C$, and

$$\frac{p}{C} = m'p^{n'} \tag{6.1}$$

as has been done on Figures 2 and 3.

Considering only the vapor pressure exerted independently by each gas dissolved in a silicate melt, it is possible to draw some interesting conclusions from the gas laws. For a series of decreasing pressures, using Henry's law and assuming a zero volume of gas phase at the initial pressure p_0, we can calculate the loss in mols of the volatile constituents per thousand grams of

[2] $p = kC$, where p is partial pressure, C is the concentration of a gas in the solvent liquid, and $p/C = k$, which is a constant for a given temperature.

solvent. Knowing the volume per mol at any given pressure (from experiment, or calculated from the gas laws) the loss in mols from the solvent gives the volume in liters of the gas phase.

If we consider two dissolved gases one of which has a very much higher vapor pressure than the other, it will be found that in general the constituent having the lower vapor pressure will make up an increasing proportion of the gas phase as the pressure diminishes, unless it is much less soluble than the constituent with the initially high vapor pressure, see Table 2.

The calculations for Z, Table 2, where $p/C_s = 100$ and p_0 is 32.5 are

TABLE 2*

CHANGE IN PROPORTION OF VOLATILES X, Y, AND Z IN GAS PHASE, WHEN REMOVED FROM MELT BY DECREASING PRESSURE, ASSUMING ALL FOLLOW HENRY'S LAW AND HAVE PHYSICAL CHARACTERISTICS OF H_2O BUT DIFFER IN SOLUBILITY

	$\frac{p}{C}$	Pressure in bars	Melt Dissolved gas left in melt $\frac{\text{gms}}{1{,}000}$	Gas phase			Ratio
				Gms	$\frac{\text{gms}}{\text{liter}}$ at 500° C	Volume in liters	
Y_0	19	550	522	0		0	
Y_1	19	377	358	164	166	1	
	19	300	285	237	117	2	
	19	222	211	311	78	4	
	19	148	141	381	47.5	8	
	19	90	85.5	436.5	22.2	16	
	19	50	47.5	474.5	14.7	32	
Y_7	19	27	25.5	496.5	7.8	64	
							$\frac{X}{Y}$
X_0	1	32.5	585	0		0	
X_1	1	32.0	576	9	9.3	1	.055
	1	31.5	567	18	9.1	2	.076
	1	30.5	547	36	8.9	4	.116
	1	28.8	518.4	66.6	8.3	8	.175
	1	25.8	464.4	120.6	7.5	16	.276
	1	21.5	387.0	198.0	6.2	32	.417
X_7	1	16.1	290.0	295.0	4.6	64	.597
							$\frac{Y}{Z}$
Z_0	100	32.5	5.85	0		0	
Z_1	100	12.5	2.25	3.60	3.55	1	.022
	100	7.7	1.39	4.46	2.15	2	.019
	100	4.4	.79	5.06	1.3	4	.016
	100	2.4	.43	5.42	.68	8	.014
	100	1.24	.22	5.63	.35	16	.013
	100	.63	.11	5.74	.18	32	.012
Z_7	100	.32	.06	5.79	.09	64	.012

* Weight of H_2O at 500° C taken from Goranson (Birch et al., 1942, p. 211 or calculated from Boyles law).

most suggestive as to the behavior that would be expected of a relatively insoluble gas in a magma. The proportion of Z in the melt decreases by 62 percent during the evolution of the first liter of gas, assuming 1 mol weighs 18 gms, and the second liter takes another 15 percent of the 0.32 mols originally present; about 77 percent of the total in the melt is thus eliminated during the initial evolution of 2 liters of gas. In contrast, where $p/C_x = 1$, the initial liter of gas evolved carries out only 1.5 percent of the total dissolved in the melt, and the second liter takes essentially the same amount, leaving 97 percent still dissolved in the melt instead of the 23 percent remaining at this stage where $p/C = 100$.

I conclude that where a melt is in contact with a three component gas phase made up of a relatively soluble, a moderately soluble, and a relatively insoluble gas a gradual decrease in pressure would result in a decrease in the percentage of the total vapor made up by the insoluble gas as smaller and smaller amounts of it are added to the vapor from the rapidly diminishing amount left in the melt, that the behavior of the soluble gas would be just the opposite; it would make up a constantly and rapidly increasing proportion of the total gas evolved, and a very much larger fraction of the portion evolved at a late stage. This is equivalent to saying that the relatively insoluble gases in the magma will be largely expelled early in the stage of gas evolution, and that the soluble gases are evolved late. This reaction depends primarily on the difference in the value of $f(p)$ in equation 6 rather than on the relative amounts of the different components initially present.

There is also the possibility that the volatiles dissolved in the melt will react in such a way that the vapor pressure compositions corresponding to certain proportions of the volatile constituents will be greater than the sum of the vapor pressures of the individual constituents if the others were not present. Under such circumstances a minimum boiling point mixture would be achieved during the evolution of gas at a given pressure and thereafter the various volatiles would come off in fixed proportions. No experimental data are available, however, that suggest the reality of this theoretical possibility.

Experimental Evidence Relating to the Sequence of Departure of Volatiles from a Magma.—The solubility of various gases common in magmatic emanations has been determined in silicate melts by a number of experimenters. The early work of Goranson (12) on the solubility of water in silicate melts of granitic composition is widely known and some of the pressure-temperature relations derived from his data are shown in Figure 1.

Tuttle and Bowen (39) greatly extended the data of Goranson and give an excellent discussion of the effect of water on the solidification of silicate melts approximating the composition of granite. The solubility of water in their albite-orthoclase-SiO_2-H_2O system at constant temperature can be readily obtained from their Figure 28 (page 58) and shows a remarkable correspondence to equation 6. For the 900° C isotherm the solubility is expressed throughout the range of pressures and concentrations shown (up to 4,000 bars and 9% H_2O) by $C = 0.04\ p^{0.65}$, and at 800° C by $C = 0.09\ p^{.55}$. Goranson's data for the solubility of water in a melt made from Stone Moun-

tain granite, at the 900° isotherm and up to 8 percent H_2O, is expressed by $C = 0.15\ p^{0.52}$, but for higher percentages of water the effect of increased pressure rapidly becomes negligible by comparison, and the regime expressed in the equation does not obtain.

Although a surprisingly large amount of water may be held in a granite melt under high pressures at a given temperature, it is apparent that a substantial amount of water must be given off from the melt if the pressure diminishes or temperature falls sufficiently to engender crystallization. At high pressures, the gas phase would be dense enough to carry a substantial amount of non-volatile material in solution.

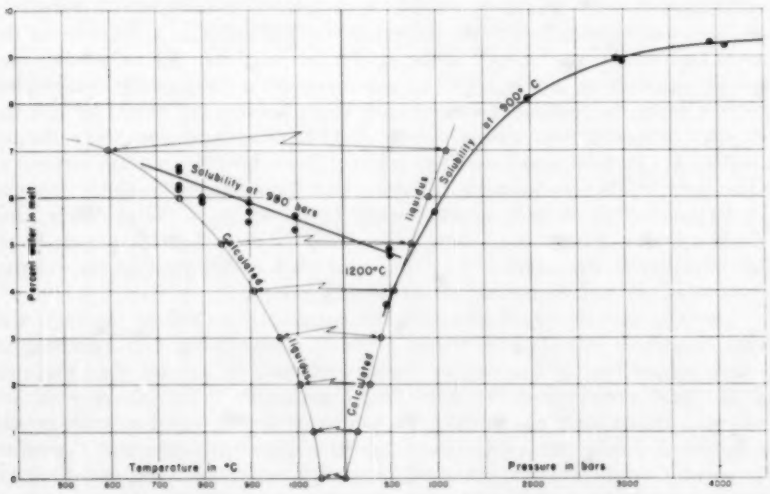

FIG. 1. Solubility of water in a granite melt as a function of temperature and pressure. Basic data from Goranson, R. W., 1931, 1932.

Kennedy (18) investigated the partial pressures of oxygen in contact with basaltic melts at different temperatures to ascertain the equilibrium of ferrous-ferric iron as a function of temperature and pressure. The ratio of FeO to Fe_2O_3 is assumed to be a function of the partial pressure of O_2, and where O_2 is constant—as in air—the ratio varies with the temperature of the melt and may be readily determined experimentally. Oxygen must also be in equilibrium with H_2 where water vapor is present and at high temperature, but no experiments were conducted using water vapor. The equilibrium dissociation of water at elevated PT conditions is known, and Kennedy shows that as a first approximation the oxygen pressure increases with the 2/3 power of the total vapor pressure of water. Very narrow limits would be imposed on the H_2 content of a gas by the reaction and ratios used. The work indicates that an increasing ferric-ferrous ratio is accompanied by

a large increase in the total vapor pressure of water as well as of oxygen in the melt at a given temperature, but with decreasing temperature at constant pressure the ferric-ferrous ratio would tend to decrease in this FeO-Fe_2O_3-H_2O system. An increase in the oxygen pressure in a crystallizing magma

TABLE 3

MOLAL SOLUBILITY OF CO_2 AND H_2O AS A FUNCTION OF THEIR PARTIAL PRESSURES IN POTASSIUM-SILICATE MELTS AT 500° C

p = pressure, C = molal concentration, i.e., $\frac{\text{mols gas}}{\text{1,000 gms melt}}$, in K_2O-SiO_2 melt*

Experiment no.**	Ratio K_2O:SiO_2	p_{CO_2}	p/C_{CO_2}	p_{H_2O}	Experiment no.	p_{H_2O}	p/C_{H_2O}
88	1:1	.5	0.159	242	71	202	19.0
86	1:1	.6	0.193	285	84	230	17.5
90	1:1	.7	0.226	353	83	233	17.4
84	1:1	9.3	2.19	230	88	242	17.2
72	1:1	9.3	2.22	288	67	250	18.3
83	1:1	9.4	2.19	233	86	285	19.5
71	1:1	9.6	2.10	202	72	288	17.3
87	1:1	9.6	2.29	353	66	326	19.5
67	1:1	26	4.94	250	90	353	23.6
66	1:1	27	5.37	326	87	353	19.2
69	1:1	27	5.25	385	69	385	19.2
Average							18.9
96	1:3	4	22.5	167	23	130	18.9
92	1:3	4	24.2	334	57	167	24.9
57	1:3	11	9.0	167	96	167	28.3
52	1:3	11	9.5	169	52	169	27.7
99	1:4	12	32.2	263	11	223	28.8
38	1:3	13	17.3	261	12	224	30.8
53	1:3	13	17.6	354	14	225	30.0
61	1:3	13	15.6	410	97	259	23.6
55	1:3	14	20.0	261	55	261	31.9
48	1:3	14	20.0	359	38	261	32.0
98	1:4	21	22.8	332	99	263	35.6
100	1:4	21	21.8	341	27	308	35.2
97	1:4	23	44.5	259	63	314	34.2
23	1:3	23	11.8	130	98	332	38.4
12	1:3	25	20.6	224	92	334	34.0
14	1:3	25	20.8	225	100	341	37.5
65	1:3	25	21.1	374	53	354	35.3
11	1:3	26	26.2	223	48	359	39.9
27	1:3	26	28.4	308	65	371	34.6
63	1:3	26	26.2	314	61	410	39.0
Average			21.54				

* Basic data from Morey and Fleisher (1940); p/C calculated by T.S.L.

** Experiment number refers to original number as given by Morey and Fleisher (1940) in their Table 5.

could profoundly effect the oxidation state of the sulfur it contained and thus perhaps its solubility and vapor pressure.

One of the few experimental investigations in which the solubility of two gases in contact with a silicate melt has been studied is that of Morey and

Fleischer (29). Potassium silicate melts of several compositions were allowed to come to equilibrium with differing amounts of carbon dioxide and water at a temperature of 500° C. When the relationship of p/C for water and for carbon dioxide is plotted, it becomes apparent that the two gases are essentially independent of one another and that the behavior of the gases with respect to a melt of 1:1 ratio of K_2O to SiO_2 is quite different from their behavior in contact with more siliceous melts. The data for p/C for

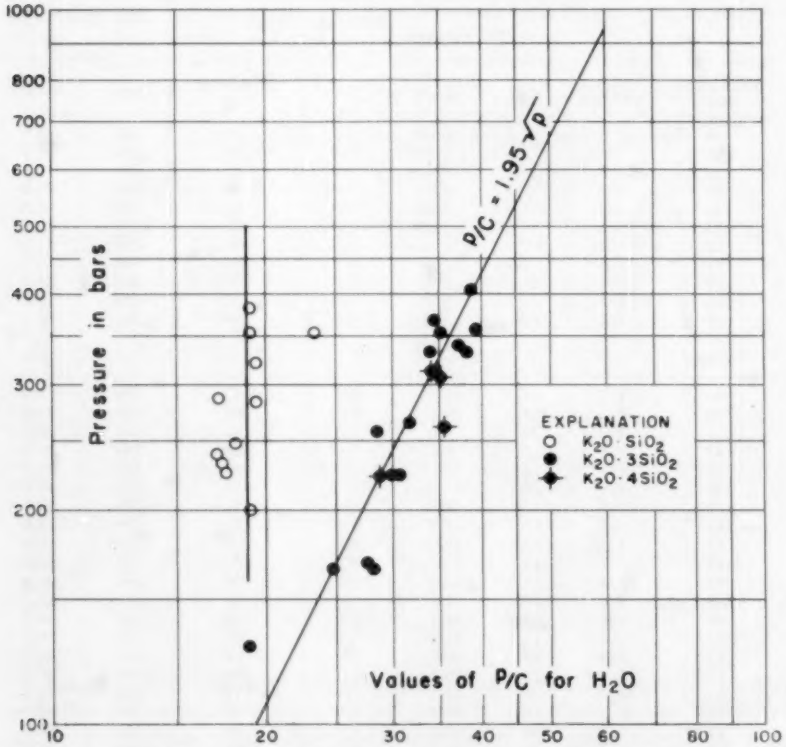

FIG. 2. Behavior of H_2O in potassium-silicate melts at 500° C and pressures from >1 to 400 At. Basic data from Morey and Fleischer, 1940.

H_2O and for CO_2 in equilibrium with different melts is plotted in Figures 2 and 3, and a summary of the data is given in Table 3. A fairly satisfactory approximation of the solubility of water in the 1:1 melt (K_2SiO_3) is given by the equation $p/C_1 = 18.8$ whereas the solubility of CO_2 quite obviously is better expressed by $p/C = mp^n$. A close approximation of its values in the range .5 atm to 30 atm is given by $p/C = 0.305\ p^{0.87}$. These relationships demonstrate clearly that for a melt of this composition with an initially high

steam pressure and a vapor pressure of some 30 atm of CO_2, release of pressure would result in a constantly increasing proportion of CO_2 in the vapor phase, and the proportion of CO_2 in the melt to water in the melt would also increase.

A plot of the p/C ratios of CO_2 and H_2O for more siliceous melts—where the ratio $K_2O : SiO_2$ ranges from 1 : 2 to 1 : 4 shows a much greater scatter of data than does the similar plot for the K_2SiO_3 system. The plot of p/C

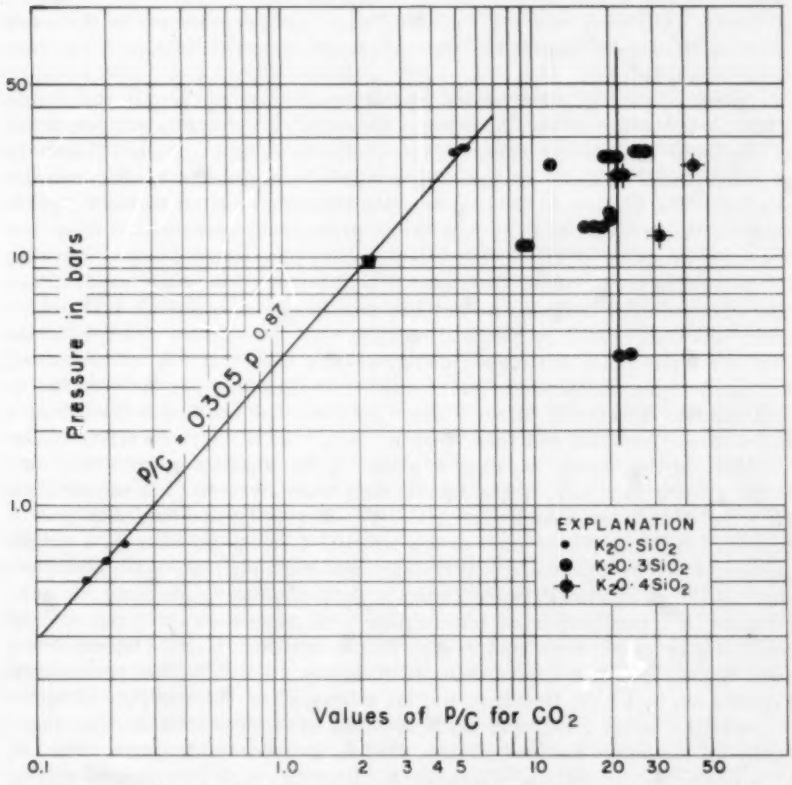

FIG. 3. Behavior of CO_2 in potassium-silicate melts at 500° C and pressures from > 1 to 400 atm. Basic data from Morey and Fleischer, 1940.

for CO_2 shows no such trend as that for the K_2SiO_3 melt. Instead, in spite of the scatter in the data there is a suggestion that for the silica-rich melt, the value for p/C for CO_2 may be a constant which approximates 21.

In contrast to the carbon dioxide, the p/C values for water show a distinct trend when plotted on log paper, and approximate the equation $p/C = 2p^{\frac{1}{2}}$. From the expressions given in Figures 2 and 3, it is apparent that CO_2

may become notably enriched in vapor phase as pressure drops, but only if the initial pressure of steam is greater by one or more orders of magnitude than that of the carbon dioxide. These conclusions accord with those of Morey and Fleischer who reason from the distribution ratios of the CO_2 and H_2O in the vapor and in the liquid that the metasilicate melts tend to retain more CO_2 than the more siliceous mixtures, and that for a given ratio of $K_2O : SiO_2$ a drop in pressure at a constant temperature will cause the composition of the vapor phase to change toward a higher content of CO_2, (29, p. 1057). However, the p/C ratios of water at low pressures in the more silicic melts suggest that if they had a low concentration of water, the converse would be true.

Another study of considerable significance is that by Wyllie and Tuttle (42) on the effect of various volatile materials on the melting temperature of different silicate systems. Albite, orthoclase, and granite (Westerly granite, Rhode Island) all behaved similarly with respect to the volatiles studied. The silicates in the granite system began to melt at higher temperatures in the presence of CO_2 than in the presence of water vapor alone, but low concentrations of HF in the volatile phase produced a marked lowering of the melting temperatures compared to that produced by water vapor alone. The effect of HCl is similar to but less pronounced than that of HF and its effect was complicated by chemical reaction with the silicates and the formation of a liquid phase not readily distinguishable from that formed by mutual fluxing between the products of reaction. The authors conclude that it is important to distinguish between those volatiles that react with the silicates to form new minerals and those that act simply as a flux. In terms of the solubility of the various volatiles it would appear that for a given pressure in the granite melt, CO_2 is less soluble than water, water is less soluble than HCl, and HCl is less soluble than HF. Wyllie and Tuttle found that granite begins to melt at a temperature as low as 610° C in the presence of 4 weight percent of HF at a pressure of 2686 bars, and conclude that small concentrations of HF in magmatic systems may be very effective in lowering the temperature of crystallization of the magma. No experiments are reported in which sulfur gases were components of the system. E. F. Osborn, however, reports (written communication of March 16, 1960) that preliminary experiments by C. W. Burnham and his colleagues on the solubility of water in pegmatite melts containing small amounts of sulfides indicate that practically all the sulfur becomes concentrated in the water-rich vapor phase, as H_2S, in equilibrium with the silicate melt. Burnham feels that the geologically important factor is not the solubility of H_2S in the magma, but whether or not there is an associated water-rich vapor phase to serve as an H_2S collector.

Field Evidence of the Change in Composition of Volcanic Emanations with Time.—Ever since Sainte-Claire Deville (8) published his memoir a century ago on the volcanic gases from Vesuvius and other Mediterranean volcanoes, controversy has continued over his conclusions that the composition of volcanic emanations varies with the time that has passed since the beginning of volcanic activity, and also with the distance of the fumaroles or hot springs from the volcanic throat (8, p. 262–270; 9, p. 60–63). The analyses indi-

cated that the gases at highest temperatures contain in addition to superheated steam relatively large proportions of H_2, CO, NH_3, CH_4, F_2, and MCl, where M is a base; water vapor, HCl, sulfur acids, and fluorides of iron and copper were more abundant in slightly cooler fumaroles; those that were still cooler contained chiefly water vapor, H_2S, and free sulfur; in the lowest temperature fumaroles and the lowest temperature "mofettes," the gases were chiefly water vapor and carbon dioxide.

Deville and Leblanc were among the first to realize that much of the gas present in volcanic emanations as ordinarily collected and analyzed must be ascribed to contamination by air and ground water. This conclusion was greatly strengthened by the careful work of Day and Shepherd and other students of the Hawaiian volcanoes, and the problem was well stated by Shepherd many years ago (35). The presence of nitrogen and free oxygen together with an appreciable amount of argon—gases almost universally present in volcanic emanations as collected—may be taken as very strong evidence of contamination by air. As Shepherd pointed out, it is most unlikely that lava could rise through a porous mass of breccia saturated with air and water without being profoundly affected by this natural absorption train. The state of oxidation of the sulfur gases is itself suggestive of the degree of contamination. Acid gases, such as SO_2 generally occur only in volcanic emanations that have clear evidence of contamination by air; on the other hand, the few analyses of hot juvenile gases in which hydrogen sulfide is present are unusually low in nitrogen, and argon, as well as oxygen.

Deville and Leblanc explained the differences in composition by assuming certain temperature controlled reactions and introduction of air: they believed that with decreasing temperature sulfur is partly oxidized to dioxide and that H_2 and CO begin to oxidize to H_2O and CO_2, the H_2O generated by oxidation in turn would react with metallic chlorides to produce hydrochloric acid, which together with the other acid gases might react with the surrounding rocks. Hydrogen sulfide was ascribed to reaction with sulfide minerals, and CO_2 in part to reaction with carbonates in the country rock, causing the gases to become depleted in halogen acids and oxidized sulfur acids but enriched in hydrogen sulfide and carbon dioxide. The apparent relationship to temperature and distance from the volcanic source thus seemed adequately explained.

Ivanov's (16) recent work, however, suggests that the chief reason for the variation in composition with temperature is the reaction of the gases with ground water rather than rocks. He concludes that high temperature fumarolic gases, which contain both water soluble and water insoluble gases (HCl, SO_2, HF, CO_2, H_2S, CH_4, B) are volcanic exhalations that have not passed through underground water; the "solfataric gases" on the other hand, which contain chiefly H_2S, CH_4, N_2, and CO_2, are the relatively low temperature residual volcanic gases that have been filtered through underground water that already contains air and other dissolved gases. The various types of hot spring waters are explained as primarily the result of hydrologic and geothermal conditions met by emanations enroute to the surface. Although I agree with most of Ivanov's ideas, I believe that a change in the composition

of deep seated emanations at the source occurs in time and profoundly affects the composition of the related thermal springs at the surface.

The mass of information collected since the pioneer work done in the middle of the nineteenth century has in part strengthened the conclusions of Deville and Leblanc, but has in part been contradictory. The belated realization that the basalt magma rising to form a lava lake in Kilauea engulfed great quantities of earlier emanation soaked talus which must add its own large, but indistinguishable, contribution to the new magma and that the convection currents in the lake continually carried down air saturated lava has detracted from the original prestige of the extremely good analyses made of Hawaiian volcanic gases. Analyses of the perennial low-temperature gas vented at Sulphur Bank near the edge of the Kilauea crater has shown that the "gas" is nearly always water vapor containing some sulfur dioxide, as would be expected from emanations highly contaminated with air and vaporized ground water. It is interesting to note, however, that just prior to the eruption of Mauna Loa in 1939, the character of the gas at Sulphur Bank changed and for the first time hydrogen sulfide was recorded (*2*). The evolution of hydrogen sulfide ceased a few weeks after the volcanic activity started, while Mauna Loa was still erupting.

The explosive eruption near Mt. Katamai which resulted in the development of the Valley of the Ten Thousand Smokes has given us much information on volcanic gases. In a recent critical study (*25*) of the earlier data together with additional information on the alteration caused by the halogen acid gases, I conclude that the earliest volcanic explosion, which shortly preceded the incandescent ash flow that resulted in the Valley of Ten Thousand Smokes, differed appreciably in composition from the gases escaping from the hot ash flow. There is substantial evidence that the earliest explosion was rich in sulfur acids, and that the fumaroles containing only the gases indigenous to the ash flow were rich in halogen acids but contained very little sulfur or carbon dioxide. It is assumed that the earliest explosion represented the culmination of increasing vapor pressure of the less soluble volatiles and was then followed by the extrusion of lava saturated at depth with the more soluble halogen acids; this magma escaping through the conduit opened by the earlier explosion must have vesiculated greatly and so yielded the incandescent froth that poured into the Valley of Ten Thousand Smokes, where its contact with the surface water of the valley immediately gave rise to fumaroles rich in super-heated steam and halogen acids.

In the 1940's volcanologists in Mexico were treated to the rare phenomenon of witnessing the birth, growth, and death of a volcano of appreciable size. Paricutin volcano was intensively studied throughout its life, and from this work we now have additional information on magmatic emanations, some of which is most germane to the present study. The basaltic lava at Paricutin rose up well into the ash cone built by the almost continuous explosive activity that characterized the life of this volcano, but broke through the side of the cone well below the top to escape in tongues of quiet basaltic lava that flowed out on the plain below for a distance of several miles. The gas phase in the cone itself was characterized by much steam and an appreci-

able amount of the sultur gases whereas the fumaroles that formed in the cooling lava contained virtually no sulfur but were rich in the volatile halides, especially ferric chloride. These halide fumaroles were given off during the consolidation of the lava but eventually gave place to steam vents lacking the halogens, and representing only vaporized meteoric water coming in contact with hot solid rock. As pointed out by Krauskopf (19), the sulfur-rich gases at the vent represented the insoluble gases given off where pressure was first released in the volcanic throat, in contrast to the halogens which were so much more soluble that they moved with the fluid lava well out beyond the breached cone. There relations are in complete harmony with the work of Tuttle, Wyllie, and Burnham noted on a previous page.

Some information as to changes in composition of ore solutions may be gleaned from a study of the literature on the composition of fluid inclusions in minerals, but only a small amount of it can be interpreted in terms of a time sequence. There seems to be general agreement that the fluid inclusions in galena are lacking in S^- or SO_4 ions but are high in chlorides of sodium, calcium, or potassium. Newhouse (32) tested the fluid inclusions in galenas from a dozen different districts scattered over Europe and North America and in several sphalerites; he found no sulfur ions in any of the inclusions and all were remarkably similar in composition. They apparently consisted largely of sodium-chloride brines with a moderate amount of calcium chloride, and he estimated the concentration as equivalent to 12 to 25 percent sodium chloride. CO_2 was not ascertained.

In contrast to the galenas, the early quartz of a gold-quartz vein of Grass Valley, California, U.S.A., contains a substantial amount of sulfate ion however (p. 130–131, 22). Using a large quantity of clean quartz from the 15th level of the Providence Mine, Lindgren found a ratio of sulfate to chloride of 16 to 1, whereas the recent work by Roedder (p. 261, 34) on several quartz samples from various mines in the district (but location in the mines unspecified) shows only 1.5 to 1 for the highest ratio of sulfate to chloride. The high ratio was in quartz not associated with galena, and it is noteworthy that in the sample where galena was an accessory mineral the ratio was very different, and there was 7 times as much chloride as sulfate.

Of perhaps somewhat greater relevance to the problem is the work of Ames (1) who gives the analyses of inclusions from galena, barite, and fluorite from the Portales mine, which are listed in the order of their deposition. His table of analyses is given below:

Sample	Ions in parts per million per kilogram of sample											
	Na	K	Na/K	Li	Rb	Cs	Cl	SO_4	Ca	Al	Mg	Cu
Portales galena	8.8	3.8	2.3	0.1	tr	tr	116.1	—	tr	100.0	70.0	50.0
Portales barite	5.0	2.8	1.8	0.1	tr	tr	25.4	—	tr	150.0	60.0	100.0
Portales fluorite	1.3	15.0	0.1	tr	tr	tr	16.8	242.1	—	100.0	60.0	7.0

The temperature of filling of the minerals indicates a temperature of 130 to 140° C for the barite and 90 to 100° C for the fluorite. A change in composi-

tion with time seems evident and the appearance of fluorine in the solution after the deposition of galena and barite is also apparent. The amount of CO_2 and H_2O present was not determined. The appearance of sulfate-sulfur in the later fluorine-bearing solutions, which are deficient in chlorine, may be a late contribution from the magma but could be due to reactions of fluorine-bearing solutions with sulfates or with sulfides in an oxidizing environment at greater depth in the hydrothermal conduit. The temperature at which the fluorite was apparently deposited suggests that the hydrothermal solutions had entered the zone of ground water.

D. E. White (41) in his thoughtful paper on the geochemistry of volcanic emanations after they leave the magma to eventually appear at the surface in the form of hot springs, shows that most present day thermal waters of volcanic origin are of the sodium chloride types; he believes that much of their load of alkalie halides is derived from volatilization of these compounds from the magma under a high vapor pressure of water, as the solubility of the halides is substantial in supercritical steam of relatively high density. White notes that some of the acid sulfate-chloride waters found in certain hot spring areas cannot be explained by the mechanism of surficial oxidation and suggests that the high sulfate content of such springs comes from sulfur that is emitted from a magma as SO_2 and SO_3 rather than as H_2S and S the more usual form of sulfur in magmatic emanations. He believes that optimum conditions for oxidation of sulfur are provided by high temperatures and relatively low pressures, and that at greater pressures and perhaps at lower temperatures, sulfur will go off as H_2S or S. Although White states specifically that the composition of volcanic waters and vapors are determined by (1) type of magma and stage of crystallization, (2) temperatures and pressures during and after departure from magma, (3) the character and quantity of mixing meteoric water, and (4) reactions with wall rock, he does not discuss the possible change in composition of the emanations at the magmatic source as a function of time—but only as a function of initial temperature and pressure.

Conclusions As to Change in Emanations with Time.—It is impossible to have accurate knowledge of the complex chemical system that is a magma, but complete information is not essential to an appreciation of some of the magmatic characteristics vitally important to understanding the genesis of hydrothermal ores. Source magmas of ores, it is generally agreed, are complex silicate melts containing dissolved volatiles; these volatiles differ individually in solubility, vapor pressure, and concentration. The solubility of all such volatiles is governed by pressure, temperature, and the composition of the melt; experimental evidence on the solubility of water in melts shows that it is much more responsive to changes in pressure than to changes in temperature. A fall in temperature in general tends to make the volatile more soluble, whereas a fall in pressure must always have the reverse effect. Changes in pressures are of two types: (a) an abrupt drop in pressure due to the emplacement of a magma from depth into a shallower hearth or to the rupturing of an impervious cover over a magma; (b) the gradual change in pressure that would accompany crystallization of an undisturbed stationary

magma, the vapor pressure of which changes in response to cooling and crystallization only; changes of the sort suggested by Morey (28) or the somewhat different changes proposed by Goranson (13).

At the start of crystallization the vapor pressure may be low, but as the amount of fluid magma diminishes the vapor pressure normally will increase, which will produce a correlative depression in the freezing point of the magma. At a late stage in the crystallization of the magma the pressure of volatiles builds up more rapidly, but if there is a transition from residual silicate melt into hydrothermal solution, eventually the decrease in equilibrium temperature that accompanies the falling temperature of the freezing point may result in decreasing the vapor pressure, and on further cooling the vapor pressure of the aqueous solution decreases with falling temperature. The maximum pressure and the stage of crystallization in which it occurs is determined by the composition of the magma itself, and after the maximum pressure is attained any further crystallization whether accompanied by a rise or fall in temperature will result only in a decrease in the pressure (27). The magmatic history suggested by Morey (27) would favor retention of metals in a batholith, a dearth of veins, and crystallization of the final residuum as pegmatites. The continued escape of volatiles, on the other hand, as suggested for conditions of type (a) above would favor expulsion of hydrothermal solutions to form veins and related deposits.

Although water vapor is chiefly responsible for the vapor pressure of a magma at any given time, the escape of the vapor phase whether it be continuous or spasmodic will diminish all the volatile constituents progressively, though at different rates.

Where multiple intrusions take place into shallow hearths or where irregular apophyses of comparatively small size are attached to a large intrusion, such bodies will have different cooling rates and different gas emission stages at a given time. In either situation, the insoluble gases from one body may be given off simultaneously with the much more soluble gases from another in a different stage of crystallization. If the gases from the two bodies follow interconnecting fractures, the emanations characteristic of the early and late stages would mix enroute to the surface. The persistence of sulfur and carbon dioxide emanations in long-lived fumaroles in volcanic fields suggest the elimination of these gases from a slowly crystallizing magma because of their relative insolubility; similarly the appearance of sulfur-poor halogen-rich emanations in fumaroles of short duration on fresh lavas and hot ash flows or in the throat of a volcano immediately following an eruption—as at Lassen Peak (7) and in Italian volcanoes (8)—all suggest the higher solubility of the halides in a magma.

Although it is quite possible that in many places conditions favored the mixing of early and late stage gases from different intrusions or from different portions of a major intrusion, one would expect that in a large number of localities a single major source of hydrothermal solutions would show an orderly sequence of emanations beginning with the least soluble and ending with the most soluble. The sequence of emanations then would follow in approximately the order CO_2 and H_2S with H_2O, or perhaps CO and SO_2

from relatively dry magmas; chlorides; and fluorides; all accompanied by water vapor, the maximum production of which would probably coincide with different minor volatiles depending on the composition of the magma, but would normally occur at approximately the time of transition from sulfur to halogen gases.

CHANGE OF SOLUTIONS BY REACTION

Theoretical Considerations.—The fluids leaving a magma will tend to reach and maintain a chemical equilibrium with the rocks through which they move, but will also tend to convert the walls adjacent to the fractures they follow into material that is inert with respect to the current emanation and will then act as a chemical insulation to protect the rock beyond from reaction. Such chemical insulation is usually more porous than the original rock and is commonly permeable to diffusing solutions. The effectiveness of diffusion, however, is inversely proportional to the square of the distance, or stated another way, the diffusion gradient changes with the square root of time.[3] The slow outward migration of the alteration envelope from the hydrothermal conduit would favor migration of the chemically active components of the emanations to higher and higher levels. At any place along the route followed from the magma to the surface where the hydrothermal fluids move through "prepared ground"—rock where physical or chemical factors exist that are known to favor localization of ore bodies—much more extensive alteration of the rocks would be expected than elsewhere (26, p. 90–103).

Pierre Laffitte has published a provocative paper in which he treats mathematically the problems of the changes in temperature of the country rock near a hydrothermal conduit, as well as the thermal regime within the hydrothermal fluid itself (20). Laffitte assumes that after the instant $t = 0$ (where t is time) there is within the hydrothermal fluid a definite gradient between the outlet at the surface and the magmatic source; and he examines the possibility that at any given point the wall rock is maintained at a constant temperature by the passing hydrothermal fluid. For these conditions a relatively simple equation expresses the change in temperature of the country rock in the neighborhood of the vein as a function of time:

$$T = T_0 \operatorname{erf}\left(\frac{x}{2\sqrt{\kappa t}}\right)$$

where T is the temperature x cm from the wall, T_0 is the initial temperature difference between the country rock and the hydrothermal fluid, κ is the diffusivity of the rock, and t is time. To maintain the temperature constant, the loss of heat by conduction must equal the amount brought to a given area

[3] Diffusion is expressed by the equation: $\frac{C_0 - C}{C_0} = \theta\left(\frac{x}{\sqrt{4Dt}}\right)$ or $C = C_0\left[1 - \theta\left(\frac{x}{\sqrt{4Dt}}\right)\right]$ where C_0 is the concentration at the interface, C is the concentration of the moving diffusion front D is the diffusion coefficient in centimeters per day and t is the time in days, and θ is the error function or "probability integral (see equation 2) of the argument enclosed in parentheses, for which tabulated values are readily available (11).

by the flow of the solution past this area. Setting the flow equal to the loss at any point below the surface gives

$$\theta = \frac{2KT_0}{C\gamma\sqrt{\Pi\kappa t}}$$

where θ is the flow of solution, K is conductivity, C is heat capacity of the solution, and γ is the geothermal gradient.

Laffitte shows that in order to maintain the walls of the vein at constant temperature while the country rock heats up the rate of flow of the hydrothermal solution must constantly diminish as the gradient in the country rock adjacent to the vein decreases. Assuming reasonable figures for conductivity and diffusivity and an initial difference in temperature of 200° C in the case he considers, he shows that if the temperature of the wall is maintained constant, then 100 days after the initial instant $t = 0$ the rate of flow past one meter transverse to the direction of solution movement would be approximately two liters per second, but that at the end of 300 years the flow would have had to decrease to approximately 0.05 liters per second. The probability that the flow would thus diminish with the $\sqrt{t}$ is negligible, and we are forced to the conclusion that instead there would be a strong tendency for the horizontal gradient to remain nearly constant in the walls close to the vein, and this in turn would require a continual rise in temperature of the walls which could result only if the higher temperatures closer to the source continually migrated upward. In short, the temperature gradient that existed initially between the surface and the magmatic source in the hydrothermal fluid would tend to continually decrease as long as the flow through the fissure was constant or increasing.

Laffitte concludes very properly from his mathematical discussion that the cooling of a hydrothermal fluid on its way to the surface must be very slight—and that the fall of temperature is not the principal cause of deposition of minerals and their gangue; he also suggests that the geologic interpretation of the solubility measured in the laboratory should strongly emphasize the variation of solubility with pressure—rather than the change with temperature. It seems to the present writer that it is also probable that the tendency towards a minimal gradient within the hydrothermal fluid would favor either a change in phase of the hydrothermal liquid or the rapid exsolution of gas on the outlet side of constrictions in the hydrothermal conduit, where a marked diminution in pressure might occur. At such places the temperature during the early history of the hydrothermal emanations might favor liquid phase or retention of gas but eventually the rising temperature of the solutions would tend to overbalance the equilibria maintained by the pressure at lower temperatures.

In the preceding section, evidence was adduced for the conclusion that the early insoluble emanations from a magma would be richest in sulfur and the carbon oxides. Such gases on reacting with the country rock should produce carbonates and sulfates or sulfides. Soluble salts of these anions would be moved out of the rock whereas insoluble salts should remain as

replacements or precipitates. Where the sulfur is present chiefly as sulfur or hydrogen sulfide, much of the iron in the rock would react with the sulfur to fix it in the form of pyrite, as was shown by Lindner and Gruner (24).

Where water vapor has a relatively high density for the existing temperature, whether above or below its critical point, a substantial amount of the soluble constituents of the rock can be carried in solution. Under these conditions, however, the solubility is usually very sensitive to changes in pressure. Although some of the base metals, especially iron and to a less extent zinc, as well as the alkaline earths, such as barium, strontium, calcium, and magnesium, are soluble in CO_2-bearing solutions in the presence of either SO_2 or H_2S, diminution of pressure quickly leads to precipitation of sulfide, sulfate, or carbonate.

In conduits followed by the early magmatic emanations, one would expect to find abundant pyrite formed by reaction of sulfur-bearing emanations with the ubiquitous indigenous iron. Also carbonates and sulfates of barium and strontium, and carbonates of other alkali earth metals would be expected where conditions favored the release of pressure on gas-charged aqueous solutions. The emanations from the magma normally would become richer in chloride and poorer in sulfur and carbonate compounds as time progressed; they would react not only with the country rock, but also with any of the reaction products of the earlier emanations with which they were in contact and were in disequilibrium.

As sulfur diminished in the emanations and consequently in the magma also, those elements remaining in the magma because of the insolubility of their sulfides in the emanations should leave as soluble chlorides in increasing quantity. When these later stage emanations came in contact with previously deposited sulfides, however, the resulting chemical disequilibrium would cause precipitation of the insoluble sulfides of the late stage metal halides; the indigenous iron that had first captured the early sulfur emanations would now be transferred to solution as a soluble halide—or bicarbonate—and migrate toward the outlet, but could be again precipitated by reaction or changes in pressure. The exchange of iron for the metals arriving late would tend to decrease the pH of the solution as two sulfurs would be released for every ferrous ion taken into solution and only one such sulfur ordinarily would be required to precipitate such newly arriving metallic ions as copper or lead (see equation 10).

Although the pH of the emanations is of major importance in determining the particular reactions that take place, the general sequence of events should be the same whether the solutions are acid or alkaline when they leave their magmatic source, as long as the sulfur appears chiefly at an early stage, separate from that of the halides. In either event, the elements tending to form insoluble sulfides in the hydrothermal solutions would tend to remain in the magma until the inhibiting sulfur was largely removed by the migratory emanations.

At high temperatures carbon monoxide and sulfur dioxide react to form carbon dioxide and sulfur vapor (between 1000 and 1200° C), and as the

temperature falls the equation

$$4CO + 2SO_2 \rightleftarrows 4CO_2 + S_2 \qquad (7)$$

progresses toward the ($4CO_2 + S_2$) side. As there are six reacting volumes on the left side of the equation and only five on the right, it is apparent that it is somewhat pressure sensitive and that increasing pressure will tend to drive it from left to right (10).

Equation 7 suggests that sulfur and carbon may leave the magma initially in the form of CO and SO_2 if the pressure is not too great, but as they cool in their ascent toward the surface, they would shift over to the form of CO_2 and S_2 or to H_2S if water were present. If the magmatic fluid were relatively dense, the presence of water vapor and alkali carbonates would result in reactions leading to the formation of thiosulfates and polysulfides. Ingerson (15, p. 728) has suggested that H_2O, H_2S, and CO_2 might be expelled early from a magma, but condensed somewhere above the magmatic chamber, there to await and precipitate late emanations carrying metal halides. It seems improbable, however, that a condensed system of H_2O, H_2S, and CO_2, would remain so long in the path of outward moving emanations.

To summarize briefly the theoretical considerations: magmatic emanations given off over a period of time would normally change in composition at the source and the substances leaving the magma would be those that were readily volatile or soluble in the emanations under the conditions of temperature, pressure, and chemical environment existing at the magmatic source; enroute to the surface, pressure sensitive reactions and to a much lesser extent, temperature sensitive reactions would take place within the emanations even though no difference in the chemical environment occurred; in general, these reactions would be oxidation, reduction, and hydrolysis, and would involve water and the oxides of carbon and sulfur; in addition to these reactions the effect of the wall rocks—especially during passage through "prepared ground" in reactive carbonate sediments—would be of major importance as the solution abstracted material from them or added elements to them; finally there would be the abrupt change in the chemical milieu occasioned by meeting magmatic emanations of a different stage from another source or the mixing with ground water.

Experimental Work Bearing on the Change in Emanations by Reaction.—Much work has been done on the synthesis of ore minerals and of considerable interest to the general thesis advanced in this paper is the work of Shouten (36), who studied the textures produced by replacing various minerals with others. He used various solutions, generally rather concentrated, either acid or basic, but always at a pressure of one atmosphere and at temperatures approximating 100° C. He was able to produce excellent replacement textures in many minerals in a surprisingly short space of time, and got excellent replacement of many of the sulfides by other sulfides and was able to reverse some of the reactions by changing the solutions. For example pyrite and marcasite were rapidly attacked by lead and copper salts; dilute solutions of $CuSO_4 + FeSO_4$ produced chalcopyrite and concentrated

solutions an impure chalcocite. Lead plumbite (K_2PbO_2) in KOH coated pyrite and marcasite with galena in a few hours. K_2CuO_2 with pyrite produced intergrowths of chalcocite and "limonite," but in the same solution chalcopyrite was replaced by chalcocite with a thin transition layer of bornite. Of interest in relation to side reactions in a basic thiosulfate solution is the experiment in which siderite was replaced by galena through the action of K_2PbO_2 and $Na_2S_2O_3$ in KOH. The siderite first changed to ferrous hydroxide which in turn was replaced by galena. Most of the replacements noted took place in one to three days and some of them in a matter of hours, and the paleosome was replaced by the metasome to depths of as much as several millimeters. The speed of the replacemnt was in general proportional to the loss of volume entailed in the change from paleosome to metasome. If an increase in volume occurred, however, it sometime caused disintegration of the paleosome and in that event replacement was accelerated, but otherwise the feeding channels were stopped up and the rate of replacement fell off rapidly or stopped.

Some of the earliest work on the replacement of pyrite by other minerals was carried on by H. N. Stokes (37, 38) in a very simple apparatus. A 4 mm I.D. sealed glass tube bent at an angle of 120° contained the charge; the upper part was water cooled and the lower part was kept at a temperature of 180° to 200° C. Slow convection kept the solution mixed and in general the charge consisted of about .2 to 1 gm of purified pyrite or marcasite to which an air-free solution saturated with CO_2 was added and heated over night to temperatures of 160° to 200°. Iron hydroxide was commonly an important product of reaction where alkaline solutions were formed but in moderately acid solutions the iron remained in solution. Cupric chloride and potassium bicarbonate reacted to form chalcocite, ferric oxide, and potassium sulfate. Lead carbonate, sodium carbonate, and marcasite yielded lead sulfide and ferric oxide together with sodium thiosulfate ($Na_2S_2O_3$), see equation 8.

$$8FeS_2 + 14PbCO_3 + Na_2CO_3 - H_2O \rightarrow 14PbS + 4Fe_2O_3 + Na_2S_2O_3 + 15CO_2. \quad (8)$$

Copper and silver salts decomposed thiosulfates on heating, yielding metallic sulfide and sulfate, but lead salts in alkaline or neutral solutions were without action on thiosulfates. The presence of thiosulfates in the end product of this reaction was unequivocally established by Stokes, but the reaction of thiosulfate with lead chloride to form lead sulfide and sodium sulfate is often cited:

$$Na_2S_2O_3 + PbCl_2 + H_2O \rightarrow PbS + Na_2SO_4 + 2HCl. \quad (9)$$

This reaction, however, requires a slightly acid solution ($pH < 5$) and free acid sufficient to decompose the $Na_2S_2O_3$ must be available before it will go forward. It is the decomposition products of the $Na_2S_2O_3$ that are responsible for the precipitation of the lead sulfide.

Zinc carbonate with potassium bicarbonate and pyrite behaved like the lead salts, forming zinc sulfide and ferric oxide, with potassium thiosulfate

in solution. Stokes found that alkali bicarbonates react with pyrite or marcasite to produce ferric oxide, alkali thiosulfate, and polysulfide. These latter experiments are important for they show that pyrite and marcasite may be completely oxidized in alkaline solutions without the intervention of free oxygen, if the sulfides generated are removed by circulation or precipitation.

In neutral or slightly acid solution Stokes found that commonly the replacement of pyrite yielded additional acid that kept the iron in solution. Cupric sulfate reacted to form both chalcocite and covellite. Lead chloride in water saturated with CO_2 yielded a solid product that contained a large amount of galena and some lead sulfate according to the reaction:

$$4FeS_2 + 7PbCl_2 + 4H_2O \rightarrow 4FeCl_2 + 7PbS + H_2SO_4 + 6HCl \quad (10)$$

$$PbCl_2 + H_2SO_4 \rightarrow PbSO_4 + 2HCl. \quad (11)$$

The experiments cited above show clearly that iron sulfide is readily replaced by galena, sphalerite, and copper sulfides in alkaline, neutral, or acid solutions, and that the iron goes into solution if the pH is not too high but that otherwise it changes to the oxide and either would remain at the site of replacement or be transported away from the site of the reaction as a colloid.

Such a reaction as that shown in equation 10 would tend toward argillic alteration of the wall rocks both at the place where the pyrite was being replaced and beyond it on the outlet side of the replacement reaction area. The spread of the argillic alteration would evidently depend on the intensity of the reactions and the reactivity of the wall rocks and their consequent effectiveness in neutralizing the acid generated in the solution. Reaction of the rapidly diffusing ions of free acids with early iron sulfide in previously pyritized altered wall rocks would cause additional sulfur to move back into the vein where it would be available for reaction with the constituents of the hydrothermal solution.

The experiments cited and others of similar nature are sufficient evidence of the readiness with which iron sulfides react with solutions of other metals to form a variety of ore minerals at temperatures and pressures appropriate to hydrothermal conditions. Shouten's experiments also show that the sulfur originally present in the pyrite may be transformed into one generation after another of new minerals as successive replacements occur.

Field Evidence of Reaction of Emanations with Wall Rocks.—From the innumerable examples of reaction between wall rocks and magmatic emanations only a few pertinent facts need be cited here. One such fact is the surprising orderliness of the paragenetic relations of ore minerals as observed in district after district; it is especially true that not only is there generally an orderly succession of minerals, but that pyrite is almost everywhere the earliest of the sulfide minerals, and that commonly there is abundant evidence of the reaction of pyrite with later ore solutions to form new sulfide minerals.

The common paragenetic relations of ore minerals led Newhouse (31) to suggest that the apparent time sequence reflected the relative solubility of the minerals in the hydrothermal solution; pyrite was early and therefore more soluble than copper sulfide, which appeared later. Newhouse believed

that with magmatic differentiation, iron, tungsten, tin, molybdenum, bismuth, zinc, copper, lead, silver, and gold became progressively less soluble in the magma and so tended to appear in that order in emanations, e.g., he assumed that solubility at the source was the cause of the sequence of minerals commonly observed in mining districts but believed that the immediate cause of precipitation was the decrease in solubility of the different minerals with falling temperature. Bandy (3) although agreeing with Newhouse on the general order of precipitation of the minerals did not agree that the late minerals were less soluble than the early minerals, and Bandy like many geologists believed that the elements in the ore deposits were all simultaneously present in a complex solution.

The general succession of sulfides as almost universally accepted was authoritatively stated by Lindgren (23). But the explanation usually offered is that the succession represents deposition of the minerals from a complex solution in the order of their solubilities—the earliest being relatively insoluble and the latest the most soluble. The contradiction implicit in assuming replacement of earlier less soluble minerals by later more soluble minerals—in the same solution—has in general been ignored.

Of some interest to the general thesis of this paper is the field evidence of precipitation of pyrite from solutions containing an excess of CO_2 with a small amount of hydrogen sulfide. Allen and Day (7, p. 112–122) in their study of the hot springs on Lassen Peak found that pyrite was a very common precipitate in the hot springs, and that the gases bubbling up from the boiling springs were very similar in composition from one to another. In general the gas was from 90 to 95 percent carbon dioxide and from .5 to 2 percent H_2S with minor amounts of H_2, CH_4, and inert gases. The hot springs that were covered by a floating mirror of pyrite such as Spring No. 9, Devils Kitchen, were slightly acid and contained almost no ferric iron but had a moderate amount of ferrous iron (from less than 5 to 150 ppm). As oxidation of hydrogen sulfide occurred at the surface and would tend to form the sulfate radical and make the iron more soluble, it is to be presumed that loss of pressure of CO_2 was the main factor in making the ferrous iron vulnerable to precipitation by the H_2S.

Hot waters highly charged with CO_2 are capable also of transporting comparatively insoluble sulfates such as those of barium and calcium until the pressure of CO_2 is released. Carles (6) has shown that the hot sulfated and bicarbonated alkaline waters of Neris-les Bains contain a soluble bicarbonate of barium in the presence of the alkali sulfates. Not only did Carles establish the presence of the barium in the natural waters but he was able to establish experimentally that substantial amounts of barium sulfate will dissolve in a sodium carbonate solution saturated with carbon dioxide under pressure, and that the barium sulfate precipitates on the release of the pressure.

Many examples could be quoted from the voluminous literature on ore deposits and hot springs, but it is sufficient to point out that the general sequence of sulfide ores is largely established by field relations and almost invariably begins with the deposition of iron sulfide, that iron may move in a

hot solution saturated with carbon dioxide in the presence of hydrogen sulfide but will precipitate as pyrite where the pressure is relieved, and that pyrite forms readily by reaction of ferrion minerals with sulfur gases.

General Conclusions as to Change in Emanations Caused by Reaction.—Theoretical considerations together with the laboratory and field evidence strongly suggest that magmatic emanations change in an orderly way during the consolidation of a magma and that the early emanations are rich in carbon and sulfur in combination with either oxygen or hydrogen, but that the sulfur gases if they do leave the magma in the form of oxides tend to react with carbon monoxide and water vapor to form hydrogen sulfide and perhaps sulfur in an intermediate oxidation state such as thiosulfate as they move into areas of lower temperature and pressure. Elements with soluble bicarbonates and sulfate such as iron and to a less extent zinc would be among the first metallic elements to leave the magma and would become fixed in areas of diminishing pressure where hydrogen sulfide would precipitate them. In advance of the movement of iron from the magma, however, the sulfur gases would themselves form pyrite by reaction with the indigenous iron of the country rocks wherever the conditions of temperature, pressure, and composition resulted in the formation of hydrogen sulfide. This early pyrite whether formed from transported iron or from iron indigenous to the country rock would furnish a source of sulfidic sulfur to react with any later magmatic emanations deficient in reduced sulfur but carrying soluble base metals whose sulfides were more insoluble in the later solutions than was iron. As magmatic consolidation progressed the sulfur gases would diminish in amount and the halogen compounds would appear in larger quantity, extracting from the magma such compounds as were more soluble in the halogen-rich fluids than in the silicate magma. When such solutions traversed rock containing the early pyrite, or mingled with early stage sulfur-bearing emanations from a different source, reactions would take place that precipitated sulfides of the late stage metals. We thus would expect an orderly succession of minerals to be present in all the veins related to the consolidation of any particular magmatic body, and would further expect that consolidation of similar magmatic bodies in other areas would show similar paragenetic relations in the ore deposits derived from them the world over.

Although it is believed that a very substantial amount of the ore of many sulfide ore deposits is generated by the reaction of late sulfide-free solutions with sulfur belonging to emanations characteristic of an earlier stage, it seems clear that some elements, especially iron and to a lesser extent zinc, can travel in hot CO_2-rich solutions that already have a high content of H_2S. It also seems probable that many ore elements may travel in thiosulfate solutions, which react under suitable conditions to yield both sulfate and sulfide with the resultant precipitation of the insoluble sulfides of metals that form soluble thiosulfates. The essential thesis of this contribution is that the composition of magmatic emanations changes slowly but continuously at the magmatic source, that metals leave the magma as soluble salts in a form quite different from that in which they are precipitated in ore deposits, that the apparent time sequence noted in the paragenesis of ore minerals represents

a real time difference in the movement of the metals from their magmatic source, and finally, that much of the ore that we see was precipitated either by sulfur coming from a different magmatic source or by sulfur that arrived at the site of deposition much earlier than the metal whose sulfide the miner exploits.

U. S. Geological Survey,
Denver, Colo.,
April 29, 1960

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NICKEL OCCURRENCES IN SOAPSTONE DEPOSITS SALINE COUNTY, ARKANSAS

PHILIP J. STERLING AND CHARLES G. STONE

ABSTRACT

Nickel of possible economic interest has recently been found in an area 15 miles west of Little Rock in Saline County, Arkansas. The nickel occurs in sulfides in talc-carbonate rocks, in iron and manganese oxides in weathered serpentine dikes, and disseminated as sulfides in unweathered serpentine.

The dikes and the talc-carbonate rock occur in deposits that are currently being mined for soapstone. Assays of samples from the soapstone pits range from a trace to 15.0 percent nickel.

INTRODUCTION

In mapping the geology of the Benton quadrangle in central Arkansas the authors noted several features of the rocks exposed in the soapstone pits of northern Saline County (Fig. 1) that were suggestive of nickel mineralization. Samples were collected and tested for nickel, cobalt, chromium, copper, and platinum, but only the percentage of nickel present seemed to justify further investigation.

Although a few cores were available from drill holes in the area, the study was based largely on the examination of the soapstone pits. Samples of the various rock units exposed in the pits were analyzed in order to isolate the nickeliferous rock. Subsequent channel sampling of the nickel-bearing rock units was then undertaken to determine the extent of the nickel mineralization.

The only previously reported nickel occurrence in Arkansas was described by Comstock (5). He states that several tons of ore containing millerite were shipped from a mine located 8 miles south of the area described in this report. The mine workings are inaccessible at the present time. Several brief reports have been written on the Saline County soapstone deposits, and although Daw (7) recognized the presence of nickel in the deposits, he indicated that only trace amounts to 0.22 percent nickel were present.

The writers are grateful to Mr. Albert J. Hess of the Milwhite Company, Houston, Texas for access to the pits and examinations of the available core samples. Mr. Norman F. Williams, State Geologist of Arkansas sponsored the study and furnished helpful advice. Mr. Drew F. Holbrook of the Arkansas Geological and Conservation Commission assisted in the field work and in writing the report. Mr. Troy W. Carney, Chemist of the Arkansas Geological and Conservation Commission, analyzed the samples.

FIG. 1. Index map showing location of nickeliferous serpentine dike area in central Arkansas.

SEDIMENTARY ROCKS

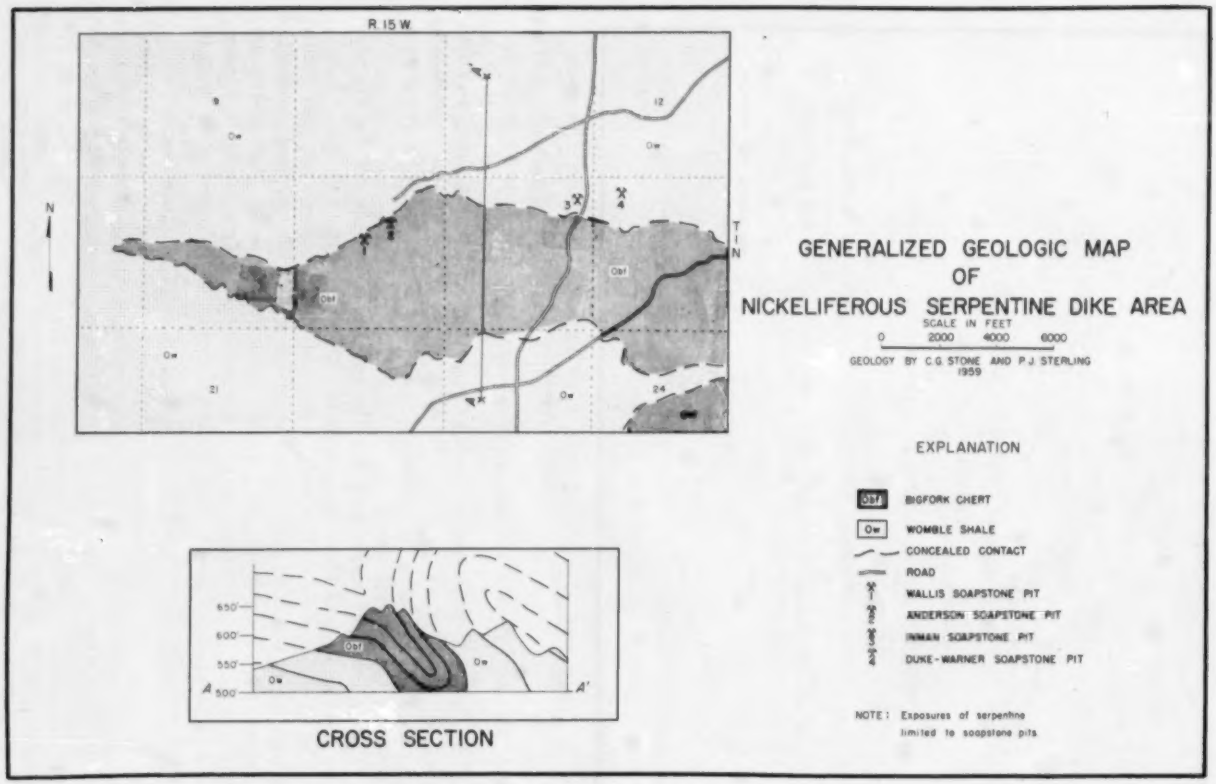
The Saline County soapstone deposits are located within the Novaculite Uplift sub-province of the Ouachita Mountains. The exposed sedimentary rocks are all of Paleozoic age. Table 1 is a measured section of the formations exposed in the general area.

The sedimentary rocks enclosing the soapstone deposits are the Womble shale and the Bigfork chert formations of Ordovician age (Fig. 2).

The Womble shale in this area consists of black to gray shale that locally contains lenses of dense black limestone and layers of siltstone and phosphatic conglomerate. Numerous milky quartz veins cut the shale. Graptolites are fairly common in the upper part of the formation. Two of the four soapstone pits examined during this study lie within the Womble shale near its contact with the Bigfork chert.

TABLE 1

System	Formation	Thickness in feet
Mississippian	Stanley shale	3,500–6,100
Mississippian-Devonian	Arkansas novaculite	365
Ordovician	Polk Creek shale	80
	Bigfork chert	195
	Womble shale	900–1,800
	Blakely sandstone	550±


R. 15 W.
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9
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GENERALIZED GEOLOGIC MAP
OF
NICKELIFEROUS SERPENTINE DIKE AREA
SCALE IN FEET
0 2000 4000 6000
GEOLOGY BY C.G. STONE AND P.J. STERLING
1959
EXPLANATION
BIGFORK CHERT
WOMBLE SHALE
CONCEALED CONTACT
ROAD
WALLIS SOAPSTONE PIT
ANDERSON SOAPSTONE PIT
INMAN SOAPSTONE PIT
DUKE-WARNER SOAPSTONE PIT
NOTE: Exposures of serpentine limited to soapstone pits
650'
600'
550'
500'
A
A'
CROSS SECTION

FIG. 2.

The Bigfork chert formation in this area consists of interbedded black chert and black siliceous shale that weathers to a gray color on the outcrop. The chert is highly shattered and has been recrystallized by metamorphism to a finely granular quartz rock resembling a siltstone. The shale is characteristically siliceous and weathers into splintery fragments. Two of the four soapstone pits lie within the Bigfork chert formation near the Womble-Bigfork contact.

IGNEOUS ROCKS

Igneous rocks are fairly common in the soapstone area. The largest intrusives are the serpentine bodies that contain soapstone deposits. These are discussed in more detail in the section on soapstone deposits. In addition to these larger masses, there are many small dikes and sills of monchiquite, ouachitite, fourchite, nepheline syenite, phonolite, syenite, trachyte, and diorite. These igneous bodies, though numerous, make up an extremely small percentage of the surface area and do not appear related to the serpentine-soapstone bodies. These smaller bodies are considered Cretaceous in age.

Quartz veins mentioned in the discussion of the Womble shale consist essentially of milky quartz with scattered chlorite inclusions, some adularia, platy calcite and dickite. Sulfides are extremely rare in these veins. The quartz veins are considered to be of hydrothermal origin (19) and are believed to be a possible source of the steatitizing solutions. The quartz veins are classified as epithermal fracture-filling veins (9). These veins commonly cut the enclosing shales and cherts and appear to surround the serpentine-soapstone bodies. The relationship of the quartz veins to the serpentine-soapstone bodies indicates that the quartz veins are younger in age. According to Engel (9) quartz veins in the Ouachitas are dated as late middle Pennsylvanian.[1] As stated before the serpentine-soapstone bodies cut the Womble-Bigfork formations (dated as middle Ordovician); therefore, it must be concluded that the intrusion of the original mass in the serpentine-soapstone area occurred between middle Ordovician and late Pennsylvanian. Thus, the intrusion is pre-orogenic or orogenic, as the Ouachita orogeny is dated as Pennsylvanian (19).

REGIONAL STRUCTURE

The sedimentary rocks of the soapstone area have been intensely folded and faulted. Generally, the folds are overturned to the south as indicated by the persistent northerly dip of the strata (Fig. 2). The soapstone deposits lie in the south limb of an overturned anticline near the Womble-Bigfork contact. The intense local crumpling of beds suggests that there is much faulting in the area, but the degree and direction of movement is difficult to establish because of poor exposures and similarity of beds.

[1] Hess (12) indicates that at Schuyler, Virginia, clear glassy lenses of quartz were found in the hanging wall above the altered ultrabasic intrusive. He states that this may represent SiO_2 lost from the ultrabasics during the last stages of steatitization. In the Saline County soapstone area, possibly some of the smaller quartz lenses on the outer edges of the soapstone deposits are of this origin; however, in most instances it can be illustrated that the quartz veins are of hydrothermal origin.

THE SOAPSTONE DEPOSITS

Since the soapstone deposits are the locus of the nickel mineralization a generalized description of them is included. The four known deposits are the Wallis, Anderson, Inman and Duke-Warner pits (Fig. 2). All but the Wallis deposit are currently being mined. In order to avoid confusion in the discussion of rock types exposed in the soapstone pits the principal types are defined as follows:

Talc	Rock containing 90 percent or more of the mineral talc.
Soapstone	Over 50 percent talc with dolomite, serpentine, and minor sulfides making up the remainder.
Serpentine	Over 60 percent of the rock is the mineral serpentine (antigorite) with appreciable dolomite and talc, and traces of sulfides.
Serpentine dikes	Over 90 percent serpentine.
Dolomite rock	Over 75 percent of the rock is dolomite with some calcite, serpentine and minor sulfides and talc.

It is believed that the irregular lense-shaped soapstone deposits occur along an east-west trending, sill-like, serpentine intrusion. This intrusion is believed to pinch, swell, and plunge, causing the soapstone deposits to appear as completely isolated bodies; however, their alignment and the presence of serpentine float and small serpentine dikes in test pits between them makes it probable they occur along a single mass. There is a roughly zonal arrangement of the principal rock units in the soapstone deposits (Fig. 3) proceeding from the sedimentary contact inward to the core as follows:[2]

1. Talcose shale or metamorphosed chert.
2. Milky quartz veins and, at some deposits, contiguous serpentine dikes.
3. Soapstone.
4. Dolomite.
5. Serpentine rock (core).

NICKEL MINERALIZATION

Positive identification of all of the nickeliferous minerals has not as yet been made, but both primary and secondary nickel mineralization are present.

The primary nickel minerals in the deposits are nickeliferous sulfides (probably nickeliferous pyrite and pyrrhotite). These sulfides occur as thin seams or stringers in dolomite rock lenses that border the Inman pit. A selected sample of this sulfide-rich dolomite rock from one corner of the pit assayed 3.1 percent nickel. Although finely crystalline sulfides are disseminated throughout the dolomite rock unit elsewhere in this pit, samples of this rock assayed less than one percent nickel. Drill cores of unweathered serpentine rocks from the Duke-Warner and Anderson deposit revealed

[2] The entire body is cut by small discordant veins of crystalline talc and calcite.

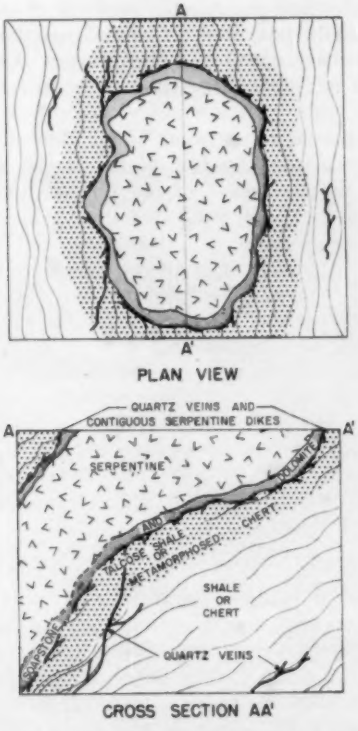

FIG. 3. Diagrammatic sketch of serpentine-soapstone body showing zonal arrangement of rock units.

similar sulfides as finely crystalline disseminations and as minute veinlets. Typical core samples of this serpentine rock from the Duke-Warner pit analyzed from 0.025 to 0.39 percent nickel and similar cores from the Anderson pit ranged from 0.05 to 0.27 percent nickel. It is probable that some of this nickel is in the silicate structure of the serpentine itself.[3]

There apparently has been some enrichment of nickel during the weathering process as the weathered rock types invariably show higher nickel content than their fresh equivalents. Secondary nickel mineralization is most pronounced in two of the rock units exposed in the soapstone pits; the partially weathered serpentine rock, and the limonitic soapstone. The partially weathered serpentine rock that contains nickel is exposed only at the Wallis and Anderson pits. Weathering in this rock has resulted in the

[3] It should be noted here that several selected samples were taken from the peridotite mass at Murfreesboro, Arkansas, and checked for their nickel content. They averaged 0.23 percent nickel. Most of this nickel is contained in silicates. Further investigation of this area is being conducted at present.

oxidation of the sulfides and possibly the removal of some carbonate leaving the serpentine essentially unaltered. Channel samples of this rock range from 0.66 to 1.50 percent nickel and the greatest thickness is exposed at the Anderson pit. It is believed that most of the nickel in this rock is associated with goethite.

The limonitic soapstone zones occur at all four of the deposits. These zones vary in thickness from 2.6 feet in the Inman pit to 26 feet in the Anderson pit. The nickel content of the limonitic soapstone varies from 0.66 to 1.22 percent and it is believed that the nickel occurs in the goethite and manganese oxides associated with this soapstone.

A thin green coating of garnierite (?) is found in the weathered dolomite zone of Inman, Duke-Warner and Anderson pits, and in weathered cores from the Duke-Warner deposit. As this mineralization occurs only sparingly, no samples of this material were analyzed.

The highest assay (15 percent nickel) obtained from any of the pits was a sample of nickeliferous iron and manganese oxides from a narrow vein in serpentine rock in the Anderson pit. These small veins are composed chiefly of crystalline talc stained by small quantities of limonite, but in the Anderson pit they contain nickeliferous iron and manganese oxides. The veins are too narrow, widely scattered and discontinuous to be important commercially.

ORIGIN

In a preliminary report without the aid of many thin sections or polished sections only a few obvious generalizations may be made concerning the origin of either the serpentine-soapstone bodies or the nickel mineralization.

Serpentine-Soapstone Bodies.—The serpentine dikes in the area are considered by the authors to be the result of automorphism of an ultrabasic intrusive. The intrusion of this ultrabasic body took place prior to or during the Ouachita orogeny (Pennsylvanian). The talc-dolomite-soapstone alteration was accomplished by the steatitization of the serpentine body, by low-temperature hydrothermal solution. The origin of the talc veins is not known but possibly are hydrothermal fracture-filling veins formed during the process of steatitization.

Nickel Mineralization.—The nickel in the sulfides and in the serpentine was probably derived from olivine, present in the original ultrabasic intrusive, during serpentization. According to Moorhouse (20) small deposits of nickel are often found in serpentine or peridotite bodies associated with differentiated sills and in isolated small intrusions. The sulfides carrying the nickel are always disseminated grains or pods that replace the serpentine. They are generally limited to the intrusive, and the nickel in them may have been derived from the olivine during its alteration to serpentine.

The nickeliferous iron and manganese oxides occur as disseminations and fracture coatings in the weathered serpentine and the limonitic soapstone. The limonitic soapstone and weathered serpentine zones owe their higher nickel content chiefly to the oxidation and residual concentration of the nickeliferous sulfides.

The oxides occurring in the talc veins are considered to have been deposited originally as sulfides from hydrothermal solutions during steatitization and later oxidized and concentrated by weathering. It is interesting to note that an assay of this nickeliferous oxide showed a zinc content of more than 1 percent. The zinc was probably introduced by these solutions.

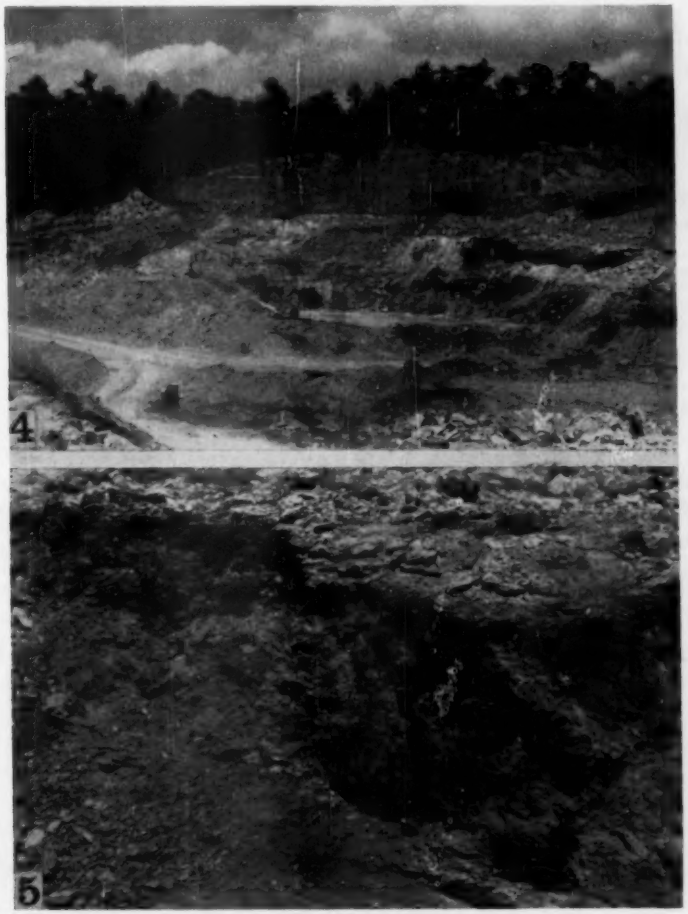

FIG. 4. Anderson pit, east face. Note sharp contact in the center of the photo between overlying Bigfork chert and soapstone-serpentine body. Black zone in the right center is a limonitic-soapstone zone that overlies the serpentine dike exposed at the base of the pit.

FIG. 5. Anderson pit at base of east wall. Soapstone (white) capping a partially weathered serpentine dike (black).

TABLE II ANALYSIS

No.	Location	Sampling method	Width of zone sampled	% Ni.	Description
1	Wallis Pit	Selected	-	1.02	Limonitic-soapstone zone.
2	"	"	-	1.20	Highly weathered serpentine dike.
3	Anderson Pit	Channel	4.3	1.5	Weathered serpentine dike.
4	"	"	2.0	0.74	"
5	"	"	6.5	1.0	"
6	"	"	5.0	1.04	"
7	"	"	5.5	0.86	"
8	"	"	2.0	1.26	"
9	"	"	2.0	1.22	"
10	"	"	8.0	1.22	"
11	"	"	4.5	1.20	"
12	"	"	29.0	0.66	"
13	"	"	20.0	0.84	"
14	"	"	4.5	0.54	Limonitic-soapstone zone overlying serpentine dike.
15	"	"	26.0	0.66	"
16	"	Selected	-	15.0	Nickeliferous manganese oxide as vein residue.
17	"	"	-	0.3	Soapstone containing sulfides.
18	Inmen Pit	Channel	3.5	0.8	Limonitic-soapstone zone.
19	"	"	5.5	0.26	" " "
20	"	"	4.0	0.20	" " "
21	"	"	2.6	0.66	" " "
22	"	"	3.5	0.8	" " "
23	"	Selected	-	3.1	Sulfide Stringer in dolomite rock.
24	"	"	-	1.45	Green encrustation on sulfide in dolomite rock.
25	"	"	-	0.38	Sulfide stringer in dolomite rock.
26	"	"	-	0.36	Sulfide stringer in soapstone.
27	"	Chip	Average sample of unit	Trace	Dolomite rock.
28	"	"	"	Trace	Soapstone.
29	Duke-Garner	Channel	3.8	0.96	Limonitic-soapstone zone.
Hole #1					
30	"	Chip sampled from core	5.0	0.39	Serpentine, sulfides common.
31	"	"	2.0	0.12	Ditto, less sulfides, darker green.
32	"	"	11.7	0.31	Serpentine, sulfides common.
33	"	"	1.3	0.16	Ditto, less sulfides.
Hole #2					
34	Duke-Garner Pit	Chip sampled from core	4.5	0.24	Weathered serpentine, limonitic.
35	"	"	3.0	0.25	Partially weathered serpentine, sulfides common, limonitic.
36	"	"	19.0	0.025	Serpentine, sparse sulfides.
37	"	"	19.0	0.09	Ditto.
38	"	"	19.0	0.04	Ditto.
39	"	"	5.5	0.27	Dolomite, stringers of serpentine and sulfides common.
40	"	"	2.6	0.02	Soapstone.
Hole #3					
41	Anderson Pit	"	1.5	0.09	Serpentine, traces of sulfides.
42	"	"	6.0	0.10	Ditto.
43	"	"	6.0	0.25	Ditto.
44	"	"	6.0	0.13	Ditto.
45	"	"	6.0	0.17	Ditto.
46	"	"	6.0	0.27	Ditto.

Sampling Methods and Assays.—Sampling techniques were adapted to the poor exposures. Three types of samples were taken: (1) selected, (2) chip, and (3) channel. Channel samples do not necessarily represent true thicknesses of units sampled, as true thickness of units was undeterminable

from pit exposures. The drill cores were chip sampled and each lithologic unit was sampled at one foot intervals.

Nickel assays (Table II) were made by Troy W. Carney, Chief Chemist of the Arkansas Geological and Conservation Commission, using colorimetric methods.

ECONOMIC CONSIDERATION

Any economic considerations of the nickel producing potential of this area would be influenced by numerous factors. The most important factor is that the exact form of the nickel-bearing mineral or minerals at present is unknown. The sulfides and oxides discussed previously are known to be nickeliferous; however, an undetermined amount of the nickel in the assays in Table II is undoubtedly tied up in the silicate structure of the serpentine. Under the best of circumstances the tenor of the prospective ore is extremely low and spotty; therefore, it is mandatory that the nickel-bearing minerals be isolated, identified, and assayed and that the amount of nickel tied up in the serpentine be determined.

The nickeliferous sulfides occur as small veinlets and minute disseminations. The nickel content of these sulfides is highly erratic and although larger more concentrated masses of nickeliferous sulfides are possible within the serpentine-soapstone bodies, thus far no appreciable quantities of concentrated nickeliferous sulfides have been found.

There is apparently a limited potential tonnage of secondary nickel in the serpentine-soapstone bodies thus discovered, due to the shallow uneven depth of weathering.

The serpentine is close to the surface and follows a definite strike but is extremely irregular in outline, pinching and swelling so that exploration would require an extensive drilling program.

Assays taken during the investigation indicate that the nickel content is not uniform throughout the various zones and such small percentages of nickel are involved that the richer zones are not easily recognizable in the field.

ARKANSAS GEOLOGICAL AND CONSERVATION COMMISSION,
LITTLE ROCK, ARKANSAS,
April 26, 1960

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DISTRIBUTION OF URANIUM ORE DEPOSITS IN THE ELK RIDGE AREA, SAN JUAN COUNTY, UTAH[1]

RUSSELL H. CAMPBELL AND RICHARD Q. LEWIS

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ABSTRACT

The Elk Ridge area of southeastern Utah contains uranium ore deposits in two lower members of the Chinle formation of Late Triassic age. Each member is mineralized in different parts of the area, and where both are present only the lower contains ore. Across the Elk Ridge area from southwest to northeast, successively younger beds lap onto the unconformity that separates the Chinle from the underlying Moenkopi formation of Triassic(?), Early and Middle(?) Triassic age. Important uranium deposits have been found only in sandstone beds of the Chinle that are in contact with the Moenkopi. Sandstone of the Chinle formation lies on the Moenkopi (or is separated from it by gray mudstone of the Chinle no thicker than the depths of most of the known paleostream channel scours) in two separate parts of the Elk Ridge area. These "favorable areas" contain all the mines and important prospects.

The ore deposits are flat-lying tabular to lenticular bodies in fluvial sandstone beds of the Chinle with fine-grained black uranium minerals chiefly interstitial to sand grains and as replacement of carbonaceous material. Most of the ore-bearing sandstone beds are discontinuous lenses intertonguing with and overlain by relatively impermeable mudstone. Contact of the host sandstone with the underlying Moenkopi seems to be a prerequisite for ore as the ore bodies are generally within a few feet of such contact areas and sandstone lenses separated from the Moenkopi by gray mudstone are generally not ore bearing.

The consistent association of ore deposits with the Chinle-Moenkopi contact suggests that mineralizing solutions were introduced into the host

[1] Publication authorized by the Director, U. S. Geological Survey.

beds from their areas of contact with the Moenkopi formation. Impermeable barriers overlying ore-bearing parts of the host sandstones were probably an important control on the deposition of ore minerals from solution. Hypofiltration of metallic constituents from ascending ore solutions may have been important. It is also possible that the overlying barriers formed traps for H_2S gas or fluid hydrocarbons and thus localized a reducing chemical environment in which ore minerals were later precipitated.

INTRODUCTION

THE Elk Ridge area of southeastern Utah contains important uranium deposits in fluvial sandstone beds at the base of the Chinle formation of Late Triassic age. The production since 1953 of significant amounts of black "unoxidized" uranium ore from several mines has demonstrated the importance of Elk Ridge as a uranium mining area. The mines and important prospects are grouped into two general favorable areas, each of which contains uranium deposits in a different member of the Chinle formation (Fig. 1). Most of the mines lie in a belt-like area that trends west to southwest across Elk Ridge and is continuous to the west into the White Canyon mining area. One mine and several prospects are in the northeastern part of the Elk Ridge area in what may be considered the southwestern continuation of the Indian Creek-Lavender Creek mining area. In both favorable areas the ore-bearing beds are in contact with rocks of the underlying Moenkopi formation of Triassic(?), Early and Middle(?) Triassic age.

The purpose of this paper is to describe the distribution pattern of the uranium deposits of the Elk Ridge area, and to discuss the stratigraphic features that probably controlled that distribution and the localization of ore bodies. Elk Ridge and the area adjacent to the northwest was mapped by the U. S. Geological Survey in the years 1953 through 1957, on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission. The writers were assisted at various times by numerous colleagues from the Geological Survey.

GENERAL GEOLOGIC SETTING

Sedimentary rocks exposed in the Elk Ridge area range in age from Pennsylvanian to Jurassic and total more than 5,000 feet in thickness (Fig. 2). The nearest exposed igneous rocks are laccolithic intrusives of hornblende andesite porphyry (21, p. 144) in the Abajo Mountains, 3 to 5 miles east of the northeastern part of the Elk Ridge area. Hunt (6, p. 82) suggests these intrusions are of middle Miocene age, but Witkind (21, p. 143) believes they may be as early as Late Cretaceous.

Elk Ridge is a high mesa cut in flat-lying to gently dipping sedimentary rocks, capped in most places by sandstone of the Moss Back member of the Chinle formation of Late Triassic age. The mesa has been intricately dissected by deep canyons that drain north, northwest, and west to the Colorado River and south and southeast to the San Juan River. A few isolated buttes of the upper part of the Chinle overlain by remnants of Wingate sandstone (also of Late Triassic age) rise above the Moss Back-capped mesa to

form such prominent landmarks as the Bears Ears and Horse Mountain. The mesa is very irregular in plan, but generally trends northeasterly across the broad gentle crest of the north-northwest-trending Elk Ridge anticline.

The Elk Ridge anticline is the most continuous of the folds along the crest of the Monument upwarp in the Elk Ridge area. The broad crestal area includes many discontinuous minor anticlines, synclines, monoclines and structural terraces. Some of these minor folds are parallel to the general northward trend of the major upwarp and others are transverse. The west flank of the upwarp has a gentle regional dip of 2° to 4° southwest. The east flank dips gently to the east and east-northeast, but is interrupted by the steep limb of the Comb monocline which locally dips as steeply as 30 degrees east. The general outlines of this steep limb are indicated on Figure 1 by the Comb anticlinal and synclinal bends.

Grabens are locally prominent, particularly across the northern part of the area and to a lesser extent in the east-central part. The grabens trend east to northeast and are bounded by vertical or steeply dipping normal faults. In many places the displacement is small, less than 100 feet, but locally displacements of several hundred feet are known. Several sets of joints are generally well developed in the more competent massive to thick-bedded sandstone units.

STRATIGRAPHY OF THE MOENKOPI AND CHINLE FORMATIONS

Only the upper part of the Moenkopi formation of Triassic(?), Early and Middle(?) Triassic age and the lower two members of the Chinle formation of Late Triassic age are discussed in detail because these beds are closely associated with the uranium ore deposits of the Elk Ridge area.[2]

The upper part of the Moenkopi formation consists of dark-brown to red thin shaly evenly bedded fine- to very fine grained sandstone, interbedded with shaly siltstone and platy to flaggy fine- to medium-grained sandstone. It averages about 250 feet in thickness and ranges from 180 to 280 feet. Siltstone and fine- to very fine grained sandstone predominate, generally in beds from less than an inch to a few feet thick, but in the middle third of the formation a few discontinuous lenses of thick-bedded fine- to medium-grained sandstone, locally as much as 40 feet thick, are commonly present. Although the rocks are generally fine grained and silt is locally abundant, clay is found in only minor amounts, chiefly in thin discontinuous beds. Fine-grained mica is locally abundant along and oriented parallel to sandstone bedding laminae. The contact of the upper part of the Moenkopi with the underlying Hoskinnini member of the Moenkopi is conformable throughout most of Elk Ridge and locally appears gradational, but in the White Canyon area to the west it is locally unconformable.

The erosional unconformity that separates the Moenkopi and Chinle formations throughout the Elk Ridge area is expressed chiefly as shallow paleostream channels in the Moenkopi filled with fluvial sandstone and mud-

[2] In this report the term Moenkopi formation is generally intended to refer only to that part of the formation above the Hoskinnini member.

Base adapted from U. S. Geological Survey Elk Ridge quadrangle, Utah, 1935

Geology modified from Elk Ridge 1NW, 1SW, 2NE, 2SE, 2NW, 2SW, 3NE, 3SE, 3SW, 4NW, and 4SW 7½ minute geologic quadrangle manu. maps by R. Q. Lewis, R. H. Campbell, and R. E. Thaden, 1954–56

FIG. 1. Generalized geologic map of the Elk Ridge area, San Juan County, Utah, showing areas favorable for uranium deposits.

EXPLANATION

Upper Triassic (and younger) — TRIASSIC AND JURASSIC

Moss Back member of the Chinle formation and younger sedimentary rocks

Lower part of the Chinle formation
Predominantly mudstone but includes some interbedded sandstone lenses and ore-bearing sandstone lenses at the base. Heavy dashed line in the southeastern part of the map area represents sandy facies not differentiated from Moss Back

UNCONFORMITY

Lower and middle(?) Triassic (and older) — PENNSYLVANIAN, PERMIAN, TRIASSIC(?) AND TRIASSIC

Moenkopi formation and older sedimentary rocks

Area favorable for uranium deposits in basal sandstone lenses of the lower Chinle
Contains virtually all basal sandstone lenses of the lower Chinle

Area favorable for uranium deposits at the base of the Moss Back
Mudstone of the lower Chinle is less than 30 feet thick and is locally absent

U / D

High-angle fault
Dashed where approximately located. U, upthrown side; D, downthrown side

Anticline
Showing trace of axial plane and direction of plunge of axis

Syncline
Showing trace of axial plane

A

Anticlinal bend
Showing trace of axial plane and direction of plunge of axis. Arrow barbed on side of steeper dip

S

Synclinal bend
Showing trace of axial plane and direction of plunge of axis. Arrow barbed on side of flatter dip

Mines from which there has been a recorded production of uranium ore

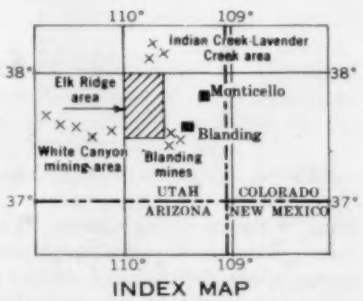
Prospect

A B C D

Lines of correlation diagrams (fig. 3) with approximate location of measured sections

15° TRUE NORTH MAGNETIC NORTH

0 5 MILES



INDEX MAP

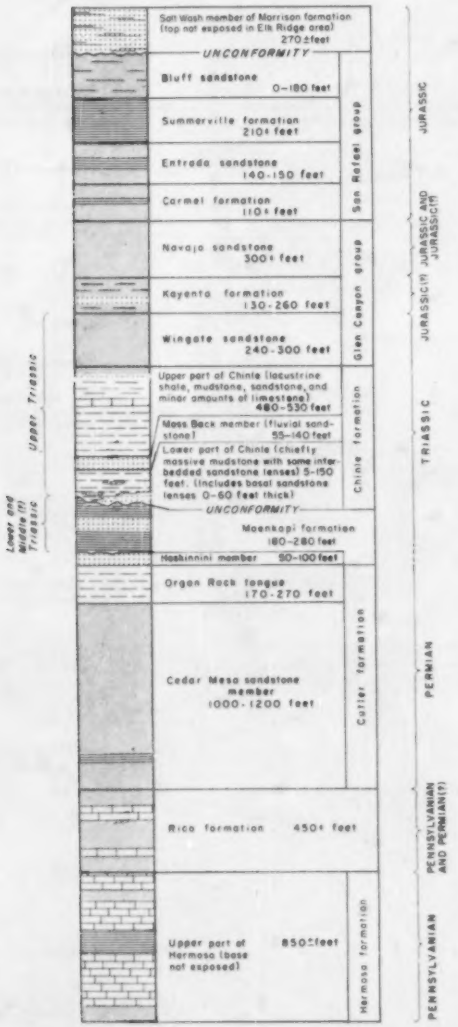

Salt Wash member of Morrison formation (top not exposed in Elk Ridge area) 270±feet
UNCONFORMITY
Bluff sandstone 0–180 feet
Summerville formation 210± feet
Entrada sandstone 140–150 feet
Carmel formation 110± feet
San Rafael group
Navajo sandstone 300± feet
Kayenta formation 130–260 feet
Wingate sandstone 240–300 feet
Glen Canyon group
Upper part of Chinle (lacustrine shale, mudstone, sandstone, and minor amounts of limestone) 480–530 feet
Moss Back member (fluvial sandstone) 55–140 feet
Lower part of Chinle (chiefly massive mudstone with some interbedded sandstone lenses) 5–150 feet. (Includes basal sandstone lenses 0–60 feet thick)
Chinle formation
UNCONFORMITY
Moenkopi formation 180–280 feet
Hoskinnini member 90–100 feet
Organ Rock tongue 170–270 feet
Cedar Mesa sandstone member 1000–1200 feet
Cutler formation
Rico formation 450± feet
Upper part of Hermosa (base not exposed) 850±feet
Hermosa formation
Upper Triassic
Lower and middle(?) Triassic
JURASSIC
JURASSIC(?) AND JURASSIC(?)
JURASSIC(?)
TRIASSIC
PERMIAN
PENNSYLVANIAN AND PERMIAN(?)
PENNSYLVANIAN

FIG. 2. Columnar section, Elk Ridge area, San Juan County, Utah.

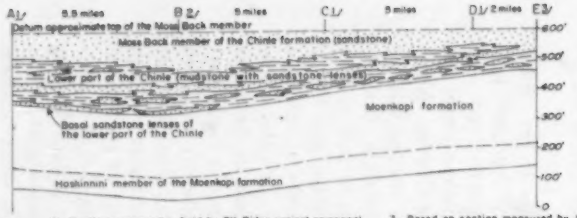
stone of the overlying Chinle. There is little evidence of regional discordance. Beds of the Moenkopi are generally parallel to the unconformity except where the banks of shallow channels filled with Chinle rocks truncate a few feet of the Moenkopi. The thickness of the Moenkopi is relatively uniform throughout the area, but the formation is generally slightly thinner—

by a few tens of feet—in the vicinity of the central favorable belt (Figs. 1, 3). The general parallelism of beds of the Moenkopi with the unconformity and the relatively uniform thickness of the Moenkopi formation suggest that pre-Chinle erosion was minor or very uniform near one horizon in the Moenkopi.

The Chinle formation is readily divisible into 3 units: the lower part of the Chinle, the Moss Back member, and the upper part of the Chinle. Stewart (18) and Johnson and Thordarson (10) have referred to the upper part of the lower unit as the Monitor Butte member of the Chinle formation, and have referred to the sandstone lenses found locally at its base as the Shinarump member of the Chinle formation. We prefer to use the informal term "lower part of the Chinle" for these rocks at Elk Ridge, as they are a continuous depositional sequence and the sandstone lenses probably are not all at the same stratigraphic horizon within the Chinle. The Chinle underlies the Wingate sandstone of Late Triassic age.

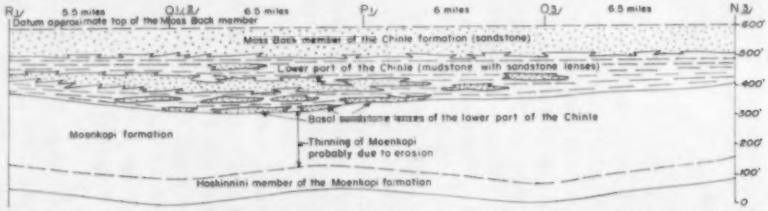
The lower part of the Chinle is predominantly massive blue to gray mudstone from 5 to 150 feet thick, most of which was probably deposited in a fluvial environment. Fluvial sandstone lenses are locally interbedded with the mudstone. In the central favorable area (Fig. 1) sandstone lenses are relatively abundant in the lower part of the lower unit of the Chinle. Many of these lenses lie at the base of the massive mudstone and occupy shallow paleostream channels cut into the underlying Moenkopi formation. Others are separated from the Moenkopi by a few feet to a few tens of feet of gray mudstone. South of the central belt sandstone is locally abundant, but is generally separated from the top of the Moenkopi by from several feet to a few tens of feet of mudstone, and the unit is slightly thinner. To the southeast, near the head of Comb Wash, sandstone is more abundant in the upper part of the lower unit of the Chinle and it intertongues with the lower part of the Moss Back member. Further southeast near the confluence of Comb Wash and Arch Canyon intermittent outcrops show sandstone, in part equivalent to the Moss Back, on and near the top of the Moenkopi. North of the central belt, sandstone lenses are rare in the lower part of the Chinle and none occur at its base. The lower Chinle thins northward and is generally about five feet thick in the vicinity of Bridger Jack Mesa. Within the northeastern favorable area (Fig. 1) mudstone of the lower part of the Chinle is generally less than 30 feet thick. It pinches out a short distance north of the map area of Figure 1.

Sandstone lenses of the lower Chinle in the favorable belt are important as host rocks for uranium deposits. To the west some of these lenses are demonstrably continuous with the ore-bearing sandstone included in the Shinarump member in the Deer Flat and White Canyon areas (20). In the Elk Ridge area, however, the basal lenses appear to represent more than one horizon within the lower Chinle. The sandstone lenses are rarely more than 20 feet thick and are commonly thinner, although locally as much as 60 feet of sandstone may be found. The basal lenses fill scours in the underlying Moenkopi, but commonly are from two to ten times as thick as the apparent depth of the scour channels. The sandstone intertongues laterally and longitudinally with massive mudstone of the lower part of the Chinle. The



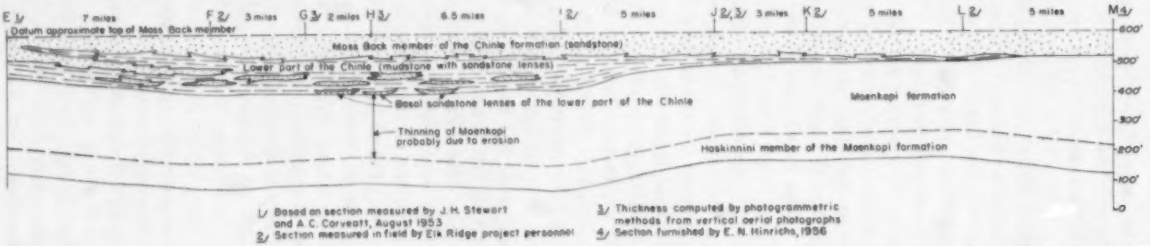
1/ Thickness computed from geologic map 2/ Section measured in field by Elk Ridge project personnel 3/ Based on section measured by J. H. Stewart and A. C. Corvcatt, August 1953

A – Correlation diagram along line A-E (see fig. 1) illustrating variations in thickness and lithology of the lower part of the Chinle formation as related to variations in thickness of the Moenkopi formation



1/ Thickness computed from geologic map 2/ Section measured in field by Elk Ridge project personnel 3/ Thickness computed by photogrammetric methods from vertical aerial photographs

B – Correlation diagram along line R-N (see fig. 1) illustrating variations in thickness and lithology of the lower part of the Chinle formation as related to variations in thickness in the Moenkopi formation



1/ Based on section measured by J. H. Stewart and A. C. Corvcatt, August 1953
2/ Section measured in field by Elk Ridge project personnel
3/ Thickness computed by photogrammetric methods from vertical aerial photographs
4/ Section furnished by E. N. Hinrichs, 1956

C – Correlation diagram along line E-M (see fig. 1) illustrating variations in thickness and lithology of the lower part of the Chinle formation and relatively uniform thickness of the Moenkopi formation

FIG. 3. Correlation diagrams, Elk Ridge area, Utah.

lenses were deposited in paleostream channels whose banks appear to have been continually built up by the development of natural levees, perpetuating the position of the depositing streams after the scour channels into the Moenkopi had been filled and buried by Chinle sediments. The paleostream channel trends are generally parallel or nearly parallel to the general trend of the favorable belt.

The sandstone lenses of the lower Chinle are composed of cross-stratified, medium- to very coarse grained, locally conglomeratic sandstone. Interstitial clay and silt are present in extremely variable amounts. The rocks grade from well-washed "clean" sandstone to very muddy sandstone. Mudstone lenses and relatively continuous thin partings are common. The contacts with the overlying and surrounding massive mudstone are generally gradational and intertonguing, but in some places mudstone fills small scours at the top of sandstone lenses. Intertonguing and gradational relationships between sandstone lenses and massive mudstone appear to prevail along channel trends as well as across them. Although sandstone beds higher in the lower part of the Chinle are generally slightly finer grained and tend to be more evenly bedded than those at the base, the differences are insufficient to allow stratigraphic assignment on the basis of composition and sedimentary structure. Stratigraphic position must be observed in the field. Carbonaceous material is locally abundant in the sandstone as carbonized logs (sparse), twigs, and tiny fragments interstitial to sand grains. Carbonized leaves have been found in the mudstone in a few localities. Interstitial blebs of asphaltite-like material and liquid hydrocarbon are locally abundant in the sandstone.

The Moss Back member of the Chinle formation overlies the lower part of the Chinle. In many places the contact is a surface of erosion, but it probably does not represent a long break in deposition. The Moss Back is a massive ledge-forming bed of fluvial sandstone and conglomeratic sandstone which is continuous throughout the Elk Ridge area. It ranges in thickness from 55 to 140 feet. In the northeastern favorable area (Fig. 1) where the lower Chinle is generally thin, channel-filling sandstone at the base of the Moss Back is locally in contact with the Moenkopi. The basal part of the Moss Back is similar in composition and sedimentary structure to the sandstone in the lower part of the Chinle. Above its base, the Moss Back is more generally fine to medium grained, contains relatively little interstitial clay or silt, and has relatively minor amounts of interbedded mudstone. The few differences between basal Moss Back and sandstone of the lower Chinle appear minor compared with their major differences from the remainder of the rocks of the area. The contact with the overlying upper part of the Chinle is conformable, locally sharply gradational or intertonguing.

The upper part of the Chinle formation consists of generally thin-bedded, even-bedded, red, pink, and gray variegated clay shales with interbedded mudstone, siltstone, shaly sandstone, and minor amounts of limestone. It is 480 to 530 feet thick. The uppermost 40 feet commonly includes from one to three beds of maroon medium- to coarse-grained sandstone, at least partly of fluvial origin, which locally intertongues with the lowermost part of the

overlying Wingate sandstone. Most of the upper Chinle was probably deposited in a lacustrine environment.

The position and trend of the central belt of basal sandstone lenses of the lower Chinle may be structurally controlled. Gentle warping was probably associated with the uplift indicated by the change in depositional environment at the unconformity. Although the Chinle-Moenkopi contact is an erosional unconformity of regional extent and represents an abrupt change in depositional environments, the thickness of the Moenkopi is remarkably uniform and the erosion surface at its top is generally parallel to underlying beds of the Moenkopi. It seems reasonable to infer, therefore, that the variations in thickness of the overlying Chinle may represent relief on the top of the Moenkopi that is largely of structural origin. The correlation diagrams (Fig. 3) suggest that basal flood-plain deposits of the lower Chinle lie in a shallow structural depression that was locally deepened by erosion.

Johnson and Thordarson (10) have discussed the westward-trending belt of basal sandstone lenses of the lower part of the Chinle in the Elk Ridge area together with its continuation into the White Canyon area as a part of the "Elk Ridge-White Canyon channel system." They suggest a source to the east or northeast, perhaps the ancestral Uncompaghre highland (10, p. 122). Studies of sedimentary structure by Poole and Williams (15, Fig. 50) indicate a westerly direction of sediment transport for sandstones of both the basal part of the lower Chinle and the Moss Back. According to Schultz (16), the clay minerals of the mudstone of the lower Chinle are chiefly montmorillonite and mixed-layer illite-montmorillonite derived chiefly from rhyolitic volcanic debris. Although Schultz observed (16, p. 504) that at least some of the volcanic material was altered after its deposition, it seems probable that most of the clay alteration took place during weathering of and transportation from the parent volcanic terrain. Pebble-, cobble-, and boulder-sized fragments of gray mudstone are abundant in some conglomeratic beds within the lower Chinle and at the base of the Moss Back. These indicate that the mudstone beds from which they were derived contained sufficient clay in a sufficiently compacted form, very shortly after deposition, to have provided coherent mudstone fragments to be broken, transported, and re-deposited as conglomerate.

Permeability and Fluid Transmissive Capacity of Rocks of the Lower Part of the Chinle and the Upper Part of the Moenkopi Formation.—The permeability and fluid transmissive capacities of the Chinle and Moenkopi formations are in large part functions of primary sedimentary features of those units. They must be considered as factors in the control of migration of ore solutions. The present conditions probably reflect fairly accurately those of the time of migration of ore solutions. Several secondary features, however, such as jointing and cementation may have been altered subsequent to ore deposition.

In general the Moenkopi, with its abundant bedding planes, joints, and relative absence of swelling clays, is considerably more permeable than the relatively massive mudstone of the lower part of the Chinle, but is less permeable than the sandstone lenses included in the lower Chinle. Except

for those at the base in contact with the Moenkopi, sandstone lenses of the lower Chinle are virtually surrounded by mudstone of extremely low permeability. The sandstones at the base are themselves separated by mudstone laterally and, at least in part longitudinally, from each other as well as from stratigraphically higher sandstone lenses. Consequently, although the sandstone lenses are themselves locally highly permeable, they lie in stratigraphic settings that should tend to isolate them from actively circulating solutions.

The present ground and surface water systems offer evidence from which permeability and fluid transmissive capacity may be inferred. The Moss Back is relatively permeable as evidenced by its capabilities as an aquifer. Mudstone of the lower Chinle is relatively impermeable, resulting in a perched water table in the Moss Back as evidenced by the large number of springs that occur at the Moss Back-lower Chinle contact. The sandstone lenses in the lower Chinle, parts of which are obviously very permeable, show no appreciable ground water flow. This may be partly a result of small areas of influent seepage, but it probably also expresses a lack of continuously connecting permeable channelways. The Moenkopi is sufficiently permeable to drain surface waters readily and is commonly used as road metal where natural drainage is poor.

The mineralogic associations of the ore deposits of the Elk Ridge area suggest that they have been protected from oxidizing conditions. The ore minerals of the Elk Ridge deposits are generally unoxidized (A. D. Weeks, written communication, 1956). Oxidized secondary minerals are common only on and near the outcrops of uraniferous deposits where ground water may circulate fairly freely within a few inches or a few feet of surface exposures of mineralized beds. The lack of appreciable oxidation of most of the Elk Ridge ores suggests that they have been protected from the circulation of oxidizing ground waters. Probably a major factor in the prevention of appreciable ground water circulation through the ore-bearing sandstone lenses is a lack of permeable connecting channelways.

The regional transmissivity of the Triassic rocks has been studied by Jobin (9). His transmissivity map (9, Fig. 39, p. 209) suggests that Elk Ridge is in an area of low regional transmissive capacity of sandstone of the lower Chinle and the Shinarump member. Additional data for the rocks of Elk Ridge and nearby areas suggest the following permeabilities and transmissive capacities for the upper part of the Moenkopi formation and the lower part of the Chinle (D. R. Jobin, written communication, 1958):

Unit	Mean permeability (millidarcies)	Transmissivity (Darcy-feet)
Upper part of the Moenkopi		0.5
Sandstone	5	
Siltstone	0.1	
Mudstone and shale	0.0	
Lower part of the Chinle		1 to 0.5
Sandstone	10 to 20[1]	
Mudstone	0.0	

[1] 175 millidarcies maximum at one place on Deer Flat.

Although the permeability of sandstone of the lower Chinle is high and that of the Moenkopi rocks is low, the transmissive capacities are of the same order of magnitude because the Moenkopi is much thicker than sandstones of the lower Chinle. The measurements and computations do not take into account such factors as the probable absence of permeable channelways interconnecting the sandstone lenses of the lower Chinle which would further reduce the transmissive capacity of the lower Chinle. Nor do they allow for the abundance of joints in the Moenkopi which should tend to increase the transmissive capacity of that unit. Jobin (written communication, 1958) also points out that in rocks of relatively low permeability faults and joints should provide a more efficient transmission system than mass permeation. In addition to faults and joints, continuous bedding planes and non-gradational formation contacts are surfaces along which transmission would be facilitated.

In summary, vertical migration of solutions through the lower part of the Chinle appears unlikely, and widespread lateral migration within the lower Chinle is less likely than migration along the underlying unconformity or through the Moenkopi.

URANIUM DEPOSITS

The uranium ore deposits in fluvial sandstone beds of the Chinle formation are flat-lying tabular to lenticular bodies, commonly elongated along the trends of shallow channels in the underlying Moenkopi. There are, of course, many irregularities in shape, but the ore bodies generally are thickest at their centers and thinner toward the margins. They range widely in size. The larger are 300 to 500 feet in length, 50 to 150 feet in maximum horizontal width, and 2 to 10 feet thick in their central parts.

In some deposits the grade of the ore is relatively uniform. More commonly, however, grade varies widely within individual ore bodies. Locally, small bodies of high-grade ore may contain as much as 5.0 percent U_3O_8, but shipments from mines have generally ranged in grade from 0.10 to 0.70 percent U_3O_8. Within some ore bodies variations in grade appear related to gradational variations in host rock lithology, but in many others irregular pods of ore are distributed without noticeable control by lithologic variations of the host rocks.

Most of the ore-bearing sandstone in the mines and prospects is black to dark gray. The ore minerals are fine grained and generally not readily identifiable in hand specimen. In many places barren or sub-ore grade material resembles ore because of the presence of abundant dark material such as fragments of carbonized wood, nonuraniferous asphaltite, and dark-colored detrital minerals. The ore is easiest and most reliably distinguished in the field by its radioactivity.

Ore Mineralogy.—With few exceptions, the ores of the Elk Ridge area are of the black or "unoxidized" (3) type, and mineralogic variations between deposits are minor. Uranium minerals, chiefly uraninite (A. D. Weeks, written communication, 1956), and associated sulfides, fill interstices in the host rock and replace many of its constituents such as clay, silt, and sand

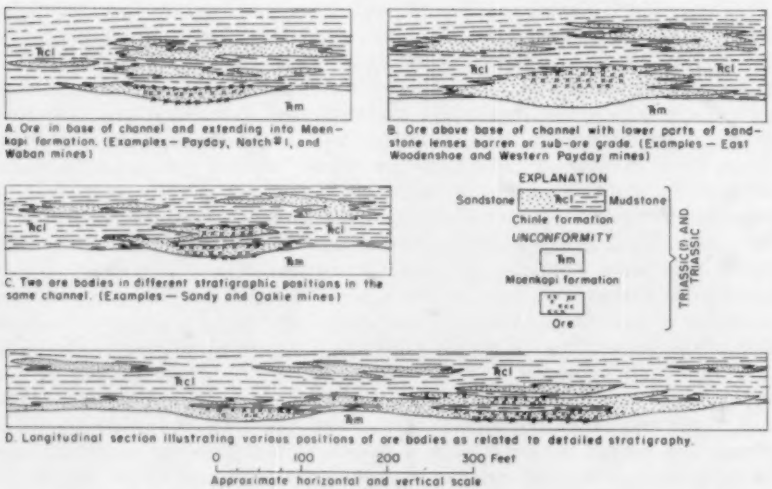
grains, carbonized wood fragments, and calcite and silica cement. Uraniferous asphaltite-like material is abundant in many mines and appears to form an important part of some ores. Fluid hydrocarbons are associated with some of the deposits. They may be either of petroliferous origin, and have migrated from underlying rocks, or may have formed virtually in place by the decomposition of vegetable matter deposited as an original constituent of the fluvial host rocks. Secondary uranium, copper, molybdenum, and cobalt minerals are locally abundant on outcrops of mineralized sandstone and as a bloom on the walls of underground workings but are rare on fresh working faces. Pyrite is the most abundant sulfide mineral associated with the uranium ores, but it is also locally abundant in areas virtually barren of uranium. Chalcopyrite is common locally in the ores.

Stratigraphic Distribution.—Although some uranium ore has been produced from other stratigraphic horizons, nearly all of the important deposits in the Elk Ridge area are in sandstone and conglomeratic sandstone lenses at the base of the massive mudstone of the lower Chinle. In the northeast part of the Elk Ridge area, a few hundred tons of uranium ore have been produced from a mine in basal sandstone and conglomeratic sandstone of the Moss Back member of the Chinle formation, but this production is minor compared to the several tens of thousands of tons produced from deposits in basal sandstone of the lower Chinle in the central belt. Sandstone lenses of the lower Chinle that are separated from the Moenkopi by intervening mudstone of the lower Chinle have been cut in many drill holes, but although they are locally mineralized, no ore deposits are known in them. Ore in the Moenkopi formation is commonly restricted to the uppermost few feet where it is almost invariably overlain by ore in basal sandstone of the Chinle. The only exception known is at the Notch No. 5 mine where a few tons of uranium ore was mined about 40 feet below the top of the Moenkopi. The Salt Wash member of the Morrison formation is known to contain important uranium-vanadium deposits in the Blanding district to the southeast, but no deposits in Salt Wash are known within the small part of the Elk Ridge area where these rocks have not been eroded. In areas adjacent to the north important deposits occur in the Moss Back, other deposits are known in arkosic facies of the Cutler formation (5, p. 63), and in lower Salt Creek a deposit occurs near the contact of the Rico formation and the Cedar Mesa member of the Cutler formation. Abundant radon, inferred to have come from the Paradox member of the Hermosa formation, was noted by R. Q. Lewis in 1953, in samples of mud from a hole drilled for oil south of the Bears Ears, and suggests possible uraniferous deposits in rocks below those exposed.

Ore may occur at one or more of several horizons within the basal sandstone of the Chinle, apparently depending greatly on the detailed local stratigraphy. In a few mines, ore occurs in the lowermost parts of the channel sandstone lenses, locally extending a few inches to two feet into the underlying Moenkopi, chiefly along fractures. In some of the deposits ore occurs in sandstone beds a few inches to a few feet thick between underlying and overlying mudstone lenses within the larger channel-filling lenses. In

many mines the basal parts of the ore bodies are from a few inches to as much as 20 feet above the top of the Moenkopi (Fig. 4).

Individual ore deposits are almost invariably overlain by rocks that are less permeable than the ore-bearing beds. In some mines the "impermeable cap" is massive mudstone. In others the cap consists of argillaceous sandstone and the change in permeability is gradational. In still other deposits, the caps are relatively thin continuous lenses or "splits" of mudstone or very argillaceous sandstone within the more permeable sandstone and conglomeratic sandstone. Even the one known ore body in sandstone of the Moss Back in the northeast part of the Elk Ridge area is capped by a relatively continuous mudstone lens within the Moss Back.


Rcl
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A. Ore in base of channel and extending into Moenkopi formation. (Examples — Payday, Notch #1, and Weban mines)
B. Ore above base of channel with lower parts of sandstone lenses barren or sub-ore grade. (Examples — East Woodenshoe and Western Payday mines)
C. Two ore bodies in different stratigraphic positions in the same channel. (Examples — Sandy and Oakie mines)
EXPLANATION
Sandstone
Mudstone
Chinle formation
UNCONFORMITY
Moenkopi formation
Ore
TRIASSIC(?) AND TRIASSIC
D. Longitudinal section illustrating various positions of ore bodies as related to detailed stratigraphy.
0
100
200
300 Feet
Approximate horizontal and vertical scale

FIG. 4. Generalized geologic sections illustrating local stratigraphic associations of uranium deposits, Elk Ridge area, Utah.

In the western part of the central belt the two Sandy mines have developed two separate ore bodies in one of the thicker of the basal sandstone lenses of the Chinle. One deposit is at the base of the host lens and is capped by a continuous mudstone split about 3 to 6 feet above the top of the Moenkopi. The other deposit, a few hundred feet to the southeast, has a base about 20 feet above the Moenkopi-Chinle contact, and is apparently capped by a gradational permeability barrier formed by a gradual upward increase in interstitial mud and, locally, calcite(?) cement. In several mines the basal parts of the host sandstone lenses are barren or only very weakly mineralized, and ore bodies were discovered at the East Woodenshoe and Western Payday mines above drifts driven in barren sandstone at the Moenkopi-Chinle contact.

Throughout the Elk Ridge area minor but noticeably increased radio-

activity is common at the Chinle-Moenkopi contact regardless of the Chinle lithology. Generally, even the relatively barren parts of basal sandstone beds of the lower Chinle contain noticeably more radioactivity than surrounding rocks. Where mudstone of the lower Chinle is in contact with the Moenkopi a thin zone (a few inches thick or less) of low abnormal radioactivity is generally present along the contact.

Areal Distribution.—The areal distribution of uranium deposits forms a distinct pattern. The favorable areas indicated on Figure 1 include all the mines of Elk Ridge. There is no obvious zoning of minerals or grade of ore in the favorable areas to indicate distribution around a local center or centers of activity. The occurrence of mineralized areas throughout the Elk Ridge and adjacent areas at various stratigraphic horizons suggests that uranium-bearing solutions circulated throughout a much larger area than that now containing the ore deposits.

In the central belt of Elk Ridge (Fig. 1) the uranium mines appear to be grouped in the eastern and western parts of the belt; however, the intervening ground has not been adequately prospected and no evidence indicates it to be less favorable than the more intensively developed parts. One ore deposit (the Horseshoe No. 1 mine) is known in the northeastern favorable area. It occurs at the base of the Moss Back in channel-filling sandstone that locally cuts through mudstone of the lower Chinle and is in contact with the underlying Moenkopi. Several prospects expose uraniferous deposits of below ore grade or size in areas where a few feet of gray mudstone separates the base of the Moss Back from the top of the Moenkopi. Only sparsely scattered weakly mineralized areas have been noted at the base of the Moss Back on outcrops and in numerous drill holes that have cut it in the central part of Elk Ridge.

The pattern of areal distribution appears directly related to the distribution of a favorable stratigraphic environment of which two parts seem essential: 1) favorable lithology—permeable fluvial sandstone beds of the Chinle that are 2) in contact with the Moenkopi-Chinle unconformity. The favorable areas (Fig. 1) are those in which these two conditions are locally met—but not necessarily everywhere present. Outside the favorable areas, however, at least one part of the favorable stratigraphic environment is generally missing.

GENESIS

The ore was deposited in chemically and physically favorable host rocks by precipitation of metallic constituents from solutions at relatively low temperatures. Alice D. Weeks of the U. S. Geological Survey believes that the mineralogic associations of the Elk Ridge deposits indicate precipitation of the uranium in a reducing environment (written communication, 1956). Syngenetic theories of deposition seem to be eliminated by evidence that the ore is appreciably younger than the host rocks.

The source of the mineralizing solutions is chiefly a matter of speculation. The ore solutions may have been relatively low-temperature end phases of solutions generated at depth by magmatic or metamorphic processes and

perhaps strong hydrothermal activity occurred in the Precambrian crystalline basement complex, the top of which is generally less than 6,000 feet stratigraphically below the ore-bearing horizons of the Elk Ridge area. The Precambrian rocks, however, are not exposed in the Elk Ridge or adjacent areas so that direct evidence of hydrothermal activity within them has not been observed. The nearby intrusive rocks of the Abajo Mountains may be younger than the ore deposits and little hydrothermal alteration is known to be associated with them (21, p. 146). There is no zoning of mineralogy or intensity of mineralization that shows direct systematic relations between the ore deposits and the exposed intrusive rocks. On the other hand, hypogene ore solutions might have been generated by the igneous processes that resulted in the intrusive rocks without being intimately associated in space or time with the actual magmatic intrusion. Many workers who have studied the Colorado Plateau sandstone deposits have considered processes by which the ore solutions may have been derived from rocks of the unmetamorphosed sedimentary section. Schultz (16, p. 504) states that at least some of the volcanic debris in the rocks of the Chinle formation was altered after its deposition and that uranium may have been derived during its devitrification. Although such a mechanism possibly was important in the derivation of ore-forming fluids on a regional scale in connection with some process such as that described by Gruner (4) as "multiple migration-accretion," it seems insufficient on a *local* scale as an immediate source for all of the uraniferous deposits of the Elk Ridge area. The present data in the Elk Ridge area are insufficient to distinguish whether the source was hypogene or supergene.

Regardless of the ultimate origin of the metallic constituents of the ore solutions (hypogene or supergene), their composition probably was modified by interaction with connate and meteoric ground waters and chemically active constituents in the rocks through which they circulated. The degree of such modification is indeterminate and might be expected to vary widely, but the widespread occurrence of similar uraniferous deposits suggests widespread circulation of relatively homogeneous ore solutions.

The uranium deposits were probably emplaced during Late Cretaceous or early Tertiary time. The Monument upwarp, which formed the Elk Ridge anticline and involved movement on the Comb monocline, may have begun to rise as early as early Paleocene time (6, p. 73 and Fig. 54). It has had no apparent effect on the distribution of the ore deposits and ore deposition may have preceded it. Because of the continuity of the central belt of the Elk Ridge deposits with the White Canyon district to the west and the mineralogical similarities of the ores of Elk Ridge and White Canyon, it seems reasonable to extrapolate data on the age and temperature of formation of the ore between the two areas. Stieff, Stern, and Milkey (19, p. 15) determined an age of 65 million years by the lead-uranium method for uraninite from the Happy Jack mine of the White Canyon district, and Coleman (1), in a study of ore from the Happy Jack mine, concludes that the temperature of formation of that deposit was probably not appreciably higher than that anticipated from computations using the normal geothermal gradient and the probable depth of burial by sedimentary rocks at that time.

Possible Paths of Solution Migration.—The habits and geologic settings of the Elk Ridge uranium deposits suggest that the mineralizing solutions entered the basal sandstone host lenses of the lower part of the Chinle from below, at areas of their contact with the underlying Moenkopi formation. The localization of many deposits below impermeable barriers may indicate deposition from ascending solutions. Upward migration might reflect a widespread ascending solution flow, or it may have been only a local component of more generally lateral movement along the Moenkopi-Chinle unconformity or through underlying rocks in a manner similar to confined ground water flow. The apparent isolation of the permeable host lenses by overlying and surrounding impermeable mudstone suggests that migration of ore solutions laterally through the lower Chinle would be unlikely except in restricted areas. The consistent association of deposits at more than one stratigraphic horizon within the Chinle with the underlying unconformity suggests solution circulation was confined beneath the mudstone of the lower Chinle.

Many uranium deposits in thicker, more continuous host beds elsewhere on the Colorado Plateau have been ascribed to deposition from solutions moving laterally through the beds that now contain the ore. In a discussion of the Happy Jack mine of the White Canyon area Isachsen and Evensen conclude (7, p. 272) that the ore-bearing fluids migrated laterally. From studies of the uranium deposits in the Shinarump member of the Chinle formation of Monument Valley, Utah, Lewis and Trimble (11) suggest that ore may have been deposited from ground waters charged with hydrothermal solutions migrating through the Shinarump which served as a partly filled aquifer. In Monument Valley, Arizona, Witkind and Thaden (22) suggest the uranium may have been deposited in the Shinarump from mineralizing solutions mixed with ground water, although Finnell (2, p. 33) suggests the deposit at the Monument No. 2 mine may have formed from ascending solutions. A study of roll ore bodies led Shawe to conclude (17, p. 241) that they formed at the crosscutting interfaces of connate water with mineralizing solutions migrating through permeable channels of the host beds. Phoenix (14) concluded that the habits of the carnotite deposits in the Salt Wash member of the Morrison formation suggest that the deposits were formed from solutions that moved laterally through the sediments and are localized where changes occurred in the rate and direction of solution movement. All of the foregoing studies concern deposits in relatively thick continuous sandstone beds. Even in the adjacent White Canyon area the host beds are generally thicker and more continuous than are those of the Elk Ridge area (13, p. 158).

In contrast with deposits in thicker, more continuous host sandstone beds, the Elk Ridge deposits are in thin discontinuous lenses of sandstone. If present, lateral permeable channelways between basal sandstone lenses of the Chinle at the same horizon must be extremely tenuous at best. Moreover, as all of the ore-bearing sandstone beds are not at the same horizon within the Chinle but are sandstones at different horizons lapping onto the unconformity, solutions migrating through the lower Chinle would have had to cross through interbedded mudstone to enter higher or lower sandstone beds.

If solutions migrated laterally through rocks of the lower Chinle, ore deposits should occur in the sandstone lenses that are separated by mudstone from the underlying Moenkopi. None of them are known to contain ore even though many are lithologically similar to the basal ore-bearing lenses and locally contain abundant carbonaceous material. Likewise, ore might be expected in the Moss Back member where it is separated from the Moenkopi by mudstone of the lower Chinle, but none is known in those areas. Thus, other paths of solution circulation in the Elk Ridge area seem more probable.

The consistent association of the ore-bearing parts of the Chinle with the Moenkopi-Chinle unconformity suggests that it was a major controlling factor in the localization of the deposits. Possibly the unconformity itself was sufficiently open to serve as the channelway for the circulation of mineralizing solutions. The low abnormal radioactivity commonly found along the Moenkopi-Chinle contact even in areas distant from known ore bodies might reflect the passage of ore solutions along the contact, but it might also reflect only the upper limit of solutions circulating in underlying rocks.

Although the permeability of the Moenkopi is low, its relative thickness and abundant bedding planes and joints indicate a fluid transmissive capacity of the same order of magnitude or possibly higher than that of the more permeable, but thinner and discontinuous basal sandstone of the lower Chinle. The occurrence of ore in the Moenkopi at the Notch No. 5 mine indicates that ore solutions circulated through those rocks at least locally. Ore solutions might well have circulated more generally through the Moenkopi, either laterally along bedding planes and the more permeable sandstone beds or upward along fractures or both.

Factors Controlling Localization.—The localization of the ore deposits of the Elk Ridge area in basal sandstone lenses of the Chinle is probably a result of two major factors: 1) mineralizing solutions had access to the sites of deposition, probably along and beneath the unconformable Moenkopi-Chinle contact, 2) the host rocks provided chemical and physical conditions favorable for the deposition of significant quantities of ore minerals from the solutions. All of these host lenses are in shallow paleostream channels cut into the underlying Moenkopi formation and filled with fluvial sediments that are generally coarser and contain less interstitial silt and clay than the interchannel Chinle rocks. The position and orientation of the ore deposits—in and generally paralleling the long dimension of the enclosing channel-filling sandstone—probably reflect the positions and orientations of the thickest and most permeable parts of the sandstone lenses.

The intimate association of many ore bodies with overlying impermeable barriers suggests a physical control by those barriers, perhaps by impounding ascending solutions. A differential diffusion mechanism, such as that termed "hypofiltration" by Mackay (12), at the sandstone-mudstone interfaces in the lower Chinle, may have increased the concentration of metallic solutes in the basal sandstone lenses by allowing the solvent to pass upward through the mudstone more readily than the solutes. Hypofiltration alone might have been responsible for the deposition of ore, but a reducing environment probably also facilitated deposition. The general association of the ore with

carbonized wood and asphaltite-like material suggests those materials provided a reducing environment in which the ore minerals were deposited.

An alternative interpretation of the manner of deposition of the ore is suggested by its association, in places, with fluid hydrocarbons and by Jensen's (8) work on the origin of the sulfur in the sulfides associated with the ore. It seems possible that fluid hydrocarbons or H_2S gas accumulated by gas or water drive in the stratigraphic traps that are now the sites of ore deposits. Such accumulations would have provided a reducing environment and might have precipitated the ore minerals at and near interfaces with underlying solutions that, during Late Cretaceous or early Tertiary time, contained metallic constituents of the ore minerals. If this were the mode of deposition, the ore solution itself need not have had an upward component of flow; the concentration gradient resulting from local precipitation may have been sufficient to cause ions to migrate within the ore solution and accumulate in the sites of deposition in sufficient quantities to form ore.

GUIDES TO PROSPECTING

The favorable areas indicated on Figure 1 should be useful guides to prospecting the general area. They indicate on a quadrangle scale the general distribution of stratigraphic environments in which the known ore bodies of the area have been found. The specific distribution of these favorable environments is best determined by direct field examination within the favorable areas to observe where individual lenses and beds of sandstone of the Chinle (including the Moss Back member) are in contact with the underlying Moenkopi rocks. Paleostream channels at the base of these sandstone beds and lenses are important guides; however, the positions and trends of channel axes may be difficult to determine because many channels are very shallow, and fluvial sandstone not only fills them but has been deposited well above the level of banks cut in Moenkopi rocks.

Most of the latent uranium ore reserves of the Elk Ridge area are probably in basal sandstone of the lower Chinle in the central belt of favorable ground indicated on Figure 1. Here the basal sandstone lenses are themselves important prospecting guides. They are thin and discontinuous and in many places do not crop out through thin blankets of colluvium and vegetation. In the northeastern favorable area (Fig. 1) a few ore bodies may be found at the base of the Moss Back member of the Chinle formation, but because the base of the Moss Back is rarely in contact with the Moenkopi formation such possible ore bodies are probably sparse. In this area, identification of paleostream channels at its base should facilitate the search for places where sandstone of the Moss Back is actually in contact with the Moenkopi. The possibility of a third "favorable area" is suggested by sandstone lenses at the base of the undifferentiated Moss Back and lower Chinle rocks along the east side of Comb Wash. However, no ore deposits have been found in these rocks. In addition, their outcrops form an intermittent linear pattern from which little can be interpreted as to areal distribution and trends of sandstone lenses. West of Comb Wash the Triassic rocks have been eroded off and east of Comb Wash exploration is difficult because the Moss Back and lower

Chinle beds are buried beneath several hundred feet of younger sedimentary rocks.

Within individual lenses of basal sandstone of the Chinle the best guides to ore are high radioactivity and visible uranium minerals. The individual ore bodies generally do not have well-defined halos of alteration or other indicators. Natural and man-made outcrops may display visible ore minerals, most commonly the colorful oxidized uranium and copper minerals. On the other hand, ore minerals, primary or secondary, are not present on the outcrops of many of the sandstone lenses that contain ore a few feet to a few hundred feet behind the outcrop. High radioactivity of outcrops is a good guide to ore in many places, and it is present at some outcrops where no visible ore minerals were found. However, nearly all of the basal sandstone lenses of the Chinle show some radioactivity higher than that of surrounding rocks and the intensity of radioactivity at outcrops is generally not an important indication of the size, grade, or distance to an ore body.

Underground in mine workings and drill holes the relation of visible minerals and radioactivity is more consistent and direct than at outcrops. Within individual mines experienced miners and prospectors, using instruments with which they are familiar, can make reasonably reliable estimates of grade on the basis of radioactivity. Although visible ore minerals are more reliable guides underground than on outcrops, abundant dark-colored sand grains and fine-grained carbonaceous material locally cause barren rock to resemble the black ore.

Much of the prospecting already done has consisted of stripping the vegetation and colluvium from the Moenkopi-Chinle contact so that it could be examined visually and the presence or absence of sandstone at the base of the Chinle could be determined. Drilling has also been successfully used in locating and delineating basal sandstone lenses of the Chinle beneath mesas capped by younger rocks. As the ore is generally in discrete bodies that occupy only a small part of the volume of the host sandstone lenses, sandstone lenses at the favorable horizon that are thick enough and extensive enough to contain ore bodies commonly must be explored physically by drilling or drifting to determine whether or not they contain ore.

Many of the Elk Ridge ore bodies in basal sandstone of the lower Chinle are separated from the base of the Chinle formation by several feet of barren sandstone. If the base of an ore body is above the back of a drift that follows the Chinle-Moenkopi contact (common exploratory practice in the area), such a drift could miss the ore completely. A few inches of barren rock may be sufficient to mask the radioactivity and other local features of nearby hidden ore bodies. Therefore, in exploring underground, provision should be made for testing a thicker basal Chinle interval than the 7 feet or so exposed for the height of a drift. If an exploratory drift follows the Chinle-Moenkopi contact, raises or drill holes at regular intervals should be used to sample several feet or even a few tens of feet of the overlying beds. Similarly, the altitude and detailed stratigraphic position of ore discovered in exploratory drill holes from the surface should be carefully noted, and subsequent underground exploration and development should not be planned solely on the

assumption that the ore body will be encountered by a drift along the Chinle-Moenkopi contact.

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MINERALOGY AND THE QUESTION OF ZONING, NORTHWESTERN ILLINOIS ZINC-LEAD DISTRICT

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ABSTRACT

A detailed study of the mineralogy and paragenesis of the zinc-lead ores of northwestern Illinois reveals that conditions of ore deposition were the same in the stratigraphically higher "crevice" deposits as they were in the deeper "flat-and-pitch" deposits. Except for an increase of galena relative to sphalerite in the crevice deposits, the minerals, their habits, and their relation to one another are the same in the two classes of deposits. In addition, spectrographic analyses show no differences in trace element content between samples of the same mineral from the different stratigraphic horizons.

It is proposed that the two classes of deposits do not represent zones of different conditions of deposition. Two possible causes of the increase of galena in the stratigraphically higher deposits are discussed.

INTRODUCTION

THE term "zoning" as applied to ore deposits is used mainly in two senses—descriptive and genetic. As a descriptive term, zoning implies the existence of belts or layers (within a vein, orebody, district, or region) differentiated, commonly, on the basis of mineral content without regard to the cause of such zoning. In the genetic sense, the belts or layers are construed to represent zones of decreasing intensity away from the source of the mineralizing solutions. Generally, temperature is thought of as the chief controlling factor and a magma as the source of the solutions. The genetic usage of the term is the classic one, and zoning to many geologists still carries genetic implications, in spite of the fact that the present trend is toward a purely descriptive meaning. An excellent discussion of the use of the term zoning may be found in a paper by Park (12).

The zinc-lead deposits of northwestern Illinois have long been known to have a rough spatial zoning. Emmons (4) interpreted this zonal arrangement in the classic sense, proposing that the shallow, predominantly galena, deposits represented an outer less intense zone of mineral deposition and the deeper, predominantly sphalerite, deposits represented the inner zone. This interpretation has been accepted by most geologists familiar with the district.

It is proposed here to show that the two classes of deposits do not represent two zones of differing depositional conditions. To this end the geology of ore occurrence and mineralogy of the deposits is discussed briefly with the addition of new spectrographic data on trace elements. The paragenesis of the ores is described in the light of the foregoing, and the problem of zoning is evaluated on the basis of the data presented.

The writer acknowledges with thanks the assistance of Juanita Witters, Associate Physicist of the Illinois State Geological Survey, who made the spectrographic determinations.

GEOLOGY OF ORE OCCURRENCE

The zinc-lead deposits of extreme northwestern Illinois are in the general vicinity of Galena. The geology of the deposits has been described (13, 3) and is summarized only briefly here. The orebodies can be separated into two classes, "flat-and-pitch" deposits and "crevice" deposits, on the basis of structure and stratigraphic position.

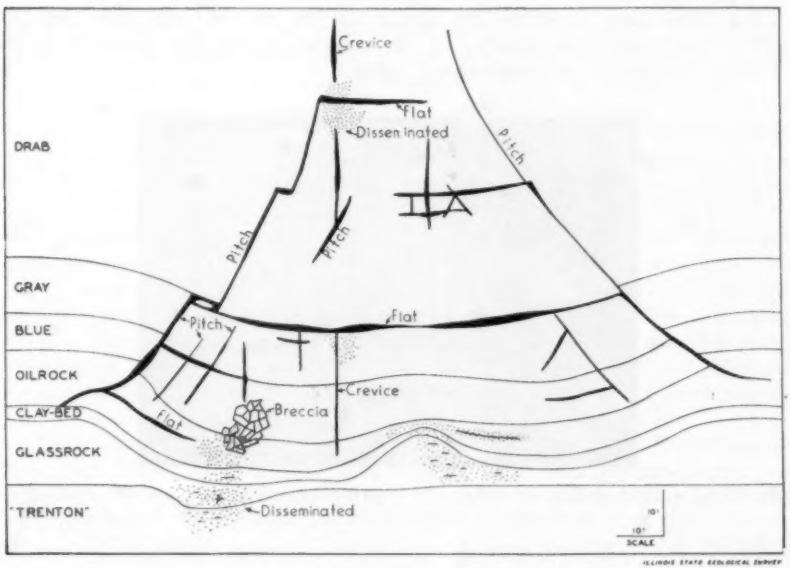

FIG. 1. Idealized cross-section of the flat-and-pitch type of deposit, showing types of ore encountered (from Willman et al., 1946).

Flat-and-pitch deposits are so-called because the ore was deposited chiefly in "flats," or open bedding planes, and in "pitches," or open inclined fractures (Fig. 1). These deposits occur in the lower part of the ore-bearing section and are associated with thin-bedded limestones and the immediately overlying medium-bedded to massive dolomites. Sphalerite is the dominant ore mineral, although galena may be locally abundant.

Crevice deposits occur in open spaces along joints in massive dolomite in the upper two-thirds of the ore-bearing section. They are much smaller than the flat-and-pitch deposits and are typically 5 to 15 feet wide, similarly thick, and a few feet to a few hundred feet long. Galena is the major ore

mineral of the deposits but in places sphalerite may predominate. As the crevice deposits generally occur at shallow depths, much of the ore is weathered.

MINERALOGY

The primary minerals of the orebodies include sphalerite, galena, pyrite, marcasite, and calcite. Chalcopyrite, millerite, and barite have been found in varying but generally small amounts in the adjacent Wisconsin zinc-lead area (6, 7) but are virtually absent in Illinois. The secondary minerals are chiefly limonite, smithsonite, and cerussite. Wad is present as small pockets and streaks in some crevice deposits.

The minerals of the crevice deposits have been discussed in some detail (3). The same minerals are found also in the flat-and-pitch deposits. Therefore, only those features of the mineralogy that are pertinent to the present discussion are summarized below.

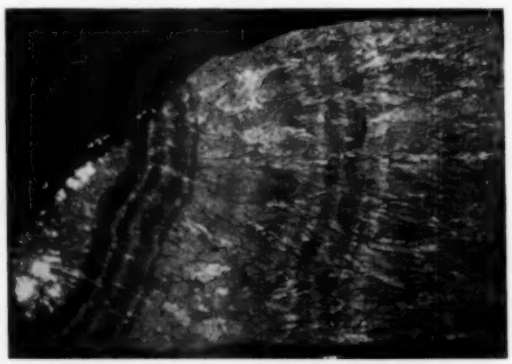

FIG. 2. Thin section of sphalerite showing typical color banding, with light-colored early zone, dark-colored middle zone, and light-colored late zone. Magnification 4 ×.

Sphalerite.—Most of the sphalerite occurs in fissures or other, more irregular cavities as aggregates of fibrous to bladed crystals. These aggregates may be radiating groups, ranging in size from a few millimeters to several centimeters, or sheets of sphalerite with the individual crystals oriented with their long axes normal to the walls of the vein or cavity. Single equidimensional crystals also occur and are found chiefly as disseminations in the argillaceous residues of the solution-attacked limestones in the lower part of the ore-bearing section.

Color bands in the sphalerite are generally parallel to the periphery of a single crystal or aggregate and range from light yellow through yellowish brown to dark reddish brown. In most specimens a partial segregation of light and dark bands reveals an early light-colored layer, a middle dark-colored layer, and a late light-colored layer (Fig. 2). The darker color bands, which

are red-orange to red in transmitted light, are generally anisotropic in thin section and, therefore, are probably wurtzite. In places where the interbanding in the dark-colored middle portion consists of very thin light and dark bands, with individual bands about 0.25 mm thick, two or more successive bands of wurtzite with isotropic sphalerite between may exhibit optical continuity and appear to be merely zones in larger crystals.

Tiny scattered purple grains of sphalerite, mostly 1 mm or less in diameter, can be observed in many sphalerite specimens in the late light-colored layer and are useful in designating isolated occurrences of light-colored sphalerite as late. The purple is apparently present as color bands in a few individual crystals of the aggregate and does not form a continuous band through the sheet of sphalerite as do the other colors. The cause of the purple is not known (see under Spectrographic Analyses). Even under relatively high magnification (225 ×) in thin section the purple is still seen as merely a shade of color and is not caused by visible inclusions.

Galena.—Galena is generally coarsely crystalline and massive. In the flat-and-pitch deposits it occurs in the central part of sphalerite veins in sheets and pods half an inch to an inch thick but may form large pods as much as 2 feet thick and several feet long. In the crevice deposits it also may be found in the central part of sphalerite veins but also, without sphalerite, as thin sheets filling fractures or as lining of caverns or open joints where the cube terminations may measure as much as 1 foot or more on an edge. Because of the generally weathered condition of the crevice deposits, the typical galena occurrence is masses of cubic crystals imbedded in a mixture of clay and dolomite sand. Minor amounts of galena also may be found intergrown with sphalerite in both the crevice and flat-and-pitch deposits or scattered in the dolomite wall rock of the crevice deposits as small masses and individual cubes generally about a fourth of an inch on an edge.

The cube is the common crystal form, but octahedral modifications are not rare. Small (2 to 3 mm) later crystals are generally octahedrons, and a few crevice lead deposits have been noted, one a few miles south of Galena and those near Guttenberg, Iowa, where the octahedron is the dominant form. Hobbs (8) mentions a two-generation crystal from the Galena area in which an earlier cube is separated from a later octahedron by a layer of marcasite.

Pyrite.—Pyrite occurs primarily in the vein walls and as a usually thin coating, a few tenths to 1 mm thick, on the vein walls between host rock and sphalerite. In places the layer of pyrite may thicken to 2 or 3 mm.

The octahedron is the common form and is the only form of pyrite found in the veins and veinlets. Cubes and cubo-octahedrons can be recognized, abundantly in places, in the very fine- to fine-grained pyrite in the vein walls. Grain size varies from 0.1 mm in the wall rock to 5 mm or more on octahedrons lining solution cavities in the host rock.

Soft, greenish-gray globules of microcrystalline pyrite, identified by means of X-ray diffraction (personal communication, W. F. Bradley) occur as concentrically layered spherical or hemispherical aggregates from 1 or 2 mm to 1 cm in diameter. Aggregates of this type have been called "melnikovite-pyrite" and assigned a metacolloidal origin (11).

Marcasite.—Marcasite occurs with pyrite in the host rock and along the veins, constituting commonly from a few to 30 percent of the pre-sphalerite FeS_2, and as fine- to coarse-grained coatings of sphalerite sheets and aggregates. Grain size of the marcasite parallels that of the pyrite with which it occurs and shows this same size range in coatings on sphalerite.

The crystals are commonly tabular; generally the base, but at some places a low dome, is the dominant form. Stubby pyramidal crystals are not uncommon. Another type of crystal frequently seen is columnar, about 0.5 mm long, and appears to be composed of diamond-shaped plates stacked one on top of another with a low dome terminating the column. Acicular crystals were found in places coating sphalerite. Twinning is common, leading to cockscomb aggregates among the tabular crystals.

A medium- to coarse-grained, fibrous variety of marcasite occurs in botryoidal aggregates that have the typical pale brass color of marcasite and contain thin shells of pyrite.

Calcite.—Calcite fills or lines open spaces in the host rock and along the centers of veins. It also occurs as veinlets cutting the ore minerals or as cement in a breccia of rock and ore. The color ranges from grayish, yellowish, or pinkish to colorless transparent. The crystal shapes also vary and single crystals may be found that contain as ghosts two or three generations with different types of terminations. Hobbs (8) described four distinct generations, beginning with scalenohedrons and ending with rhombohedrons. According to Hobbs, the first two stages are scalenohedral, with a cloudy yellow to pink color, and contain inclusions and coatings of marcasite. The calcite of the last two stages is clear; crystals of stage three are scalenohedral and those of stage four are rhombohedral.

SPECTROGRAPHIC ANALYSES

Sphalerite.—Spectrographic analyses of sphalerite, hand picked under the binocular microscope from specimens from different orebodies and from different parts of individual orebodies, are shown in Table 1. The analyses indicate that the dark and light portions of the sphalerite sheets contain the same trace elements but that the middle dark portions contain more iron, manganese, and germanium, and the early and late light colored portions contain more cadmium. The differences are not striking in every instance, but this is probably because the light and dark portions do not necessarily represent a clean-cut separation of light and dark color bands, as shown by Figure 2.

Specimens from the Bautsch orebody show a fairly good separation of color bands between the dark and late light-colored portions and, as shown in Table 1, a striking difference in the amounts of the trace elements. The early yellow sphalerite from the Appleton orebody, specimen T-32, is also a sharp color differentiate, containing sphalerite of a very light color, and it shows a correspondingly small amount of iron, manganese, and germanium.

The other trace elements show no systematic variation. Copper appears to be concentrated in the late light-colored sphalerite, but on comparing in-

Table 1

Spectrographic Analyses of Sphalerite

Sample No.*		Mine Name	Type of Deposit	Cd %	Cu %	Ge %	Fe %	Pb %	Mn %	Ag %	Cr %	V %
						Early light-colored						
31	(B)	Graham-Snyder †	F. & P.	0.18	0.0015	0.004	0.43	0.014	0.006	0.0014	0.001	n.d.
32	*	same	same	0.19	0.0014	0.004	0.36	0.012	0.005	0.0016	0.001	0.001
41-42		Graham-Snyder	F. & P.	0.13	0.0006	0.005	0.50	0.016	0.007	0.0009	0.001	n.d.
43-44	(D)	Graham-Snyder	F. & P.	0.28	0.0006	0.003	0.35	0.015	0.004	0.0006	0.001	0.001
55-56		Appleton	Crevice	0.28	0.0013	n.d.	0.14	0.012	0.001	0.0004	0.001	n.d.
						Middle dark-colored						
19	(A)	Bautsch	F. & P.	0.11	0.0037	0.038	1.42	0.104	0.013	0.0009	0.001	0.001
20		same	same	0.12	0.0028	0.028	1.15	0.076	0.012	0.0012	0.001	0.001
21		Bautsch	F. & P.	0.20	0.0024	0.022	0.99	0.116	0.010	0.0029	0.001	0.001
22		same	same	0.09	0.0028	0.028	1.14	0.086	0.012	0.0002	0.001	0.001
33-34	(B)	Graham-Snyder	F. & P.	0.16	0.0008	0.012	0.56	0.040	0.009	0.0004	0.001	n.d.
39-40	(C)	Graham-Snyder	F. & P.	0.17	0.0012	0.024	0.62	0.032	0.010	0.0003	0.001	n.d.
45-46	(D)	Graham-Snyder	F. & P.	0.20	0.0005	0.019	0.50	0.039	0.007	0.0001	0.001	n.d.
51-52	(E)	Smith no. 1	Crevice	0.09	0.0015	0.021	0.54	0.110	0.008	0.0001	0.001	n.d.
53-54		Appleton	Crevice	0.09	0.0005	0.018	0.52	0.032	0.009	0.0001	0.001	n.d.
						Late light-colored						
27-28		Bautsch	F. & P.	0.21	0.0051	0.001	0.27	0.008	0.002	0.0042	0.001	0.001
29-30	(A)	Bautsch	F. & P.	0.44	0.0068	0.001	0.28	0.032	0.002	0.0300	0.001	0.001
35	(B)	Graham-Snyder	F. & P.	0.22	0.0009	0.001	0.30	0.014	0.004	0.0006	0.001	0.001
36		same	same	0.19	0.0010	0.003	0.35	0.012	0.005	0.0002	0.001	0.001
37-38	(C)	Graham-Snyder	F. & P.	0.21	0.0009	0.002	0.30	0.010	0.003	0.0003	0.001	n.d.
47-48		Graham-Snyder	F. & P.	0.32	0.0011	0.001	0.35	0.022	0.005	0.0009	0.001	0.001
49-50	(E)	Smith no. 1	Crevice	0.14	0.0005	0.009	0.39	0.110	0.007	0.0001	0.001	n.d.
57-58		Dooling	Crevice	0.38	0.016	0.002	0.25	0.013	0.002	0.0003	0.002	n.d.
59		Little Giant	Crevice	0.26	0.0010	0.001	0.30	0.110	0.003	0.0028	0.001	0.001
						OTHERS						
60		Dooling (purple grains)		0.42	0.021	0.001	0.16	0.014	0.001	0.0001	0.001	n.d.
61		N. Central Ill. Concretion in Penn. shale		0.14	0.032	n.d.	0.42	0.011	0.002	n.d.	0.001	0.001
		Limits of detection		0.01	0.0005	0.001	0.001	0.001	0.001	0.0001	0.001	0.001

* Single sample nos. indicate pairs of samples from same hand specimen when indicated by "same" for the second sample of the pair.

† Flat and pitch

n.d. - not detected. This means that the element is not present above the limit of detection for the specific analytical method used. It should be emphasized that, for any one element, there may be very little difference between an amount reported as "n.d." and an amount shown as present at the limit of detection.

Elements not detected and their limits of detection in percent: Sb (0.01), As (0.05), Ba (0.0002), Be (0.0001), Bi (0.001), B (0.001), Co (0.001), Ga (0.002), Au (0.002), In (0.005), Hg (0.1), Mo (0.003), Ni (0.002), Nb (0.03), Pd (0.001), P (0.2), Pt (0.01), K (0.2), Rb (no estimate, Fe interference), Sr (0.01), Ta (0.5), Tl (0.1), Sn (0.003), Ti (0.004), W (0.1), Zr (0.02).

The method of numbering the samples reflects the manner of sample preparation. Each odd-even pair from 31 through 58 is from a single color layer on one hand specimen, with the individuals of each pair from opposite ends of the specimen. Most of these pairs were then combined, as indicated by the double sample numbers, but a few were analyzed separately to check the evenness of distribution of the minor elements within single color zones. Those analyzed separately are designated in the table by single numbers and the word "same" for the second sample of each pair. Samples 59 through 61 are single samples from different hand specimens.

The capital letters, A, B, C, D, and E, refer to hand specimens from which samples of more than one color layer were obtained. For instance, hand specimen (B) is represented by samples 31 and 32 of the early yellow layer, sample 33-34 of the middle dark-colored layer, and samples 35 and 36 of the late yellow layer. In the main, these hand specimens each contained a fairly thick sheet of sphalerite and generous amounts of the different color layers.

dividual samples, results are erratic. For example, specimens A and B contain more copper in the light-colored portions, but specimens C and E contain more in the dark-colored portions. In some instances, lead and silver show large variations within one color band from the same hand specimen and are probably present as impurities. Note especially sample pairs 19–20 and 21–22. Chromium and vanadium are present in amounts too small to be significant.

It is interesting to note that Kutina (9) found a similar distribution of trace elements among color bands of sphalerite from Belgium and Poland. Iron, manganese, and germanium were concentrated in the darker bands and cadmium in the lighter bands.

Another point of interest is that there are no systematic differences in trace element content between orebodies of different type. Differences do occur but they cannot be correlated with stratigraphic position or structural type of orebody. For example, in the late yellow sphalerite, the highest cadmium value (.44 percent) is shown by a sample from a flat-and-pitch deposit, but the next highest (.38 percent) is from a crevice deposit. The same lack of systematic variation with type of deposit is found in the other elements.

The late purple sphalerite was analyzed to determine a possible cause for the odd color. Sample 60, which consisted of hand-picked purple grains from sphalerite showed no trace elements different from the other sphalerites but did show an abnormal amount of copper and a little more cadmium than the general average. The small difference in copper content between the purple grains and the whole Dooling sample is probably due in part to failure to make a clean separation of the purple grains. The individual fragments of the separated purple sample always unavoidably had some light yellow sphalerite clinging to them, and the analyzed sample was probably about two-thirds purple and one-third yellow.

Recalculating the copper content of the purple sample to correct for this dilution, the uncontaminated purple sphalerite would contain .032 percent copper. If all the copper in the complete Dooling sample were contained in the purple grains which appear to form about 20 percent of the whole sample, the copper content of the whole sample should be .006 percent. As it is considerably higher than .006 percent, some of the copper must be in the yellow sphalerite. On the basis of the above calculations, the yellow sphalerite contains .010 percent copper, and the purple contains three times as much. A concentration of copper is therefore a possible contributor to the purple color.

The last entry in Table 1 is an analysis of a sample of sphalerite from a vein in an ironstone concretion found in an exposure of Pennsylvanian shale in Bureau County, north central Illinois. Presumably the sphalerite was deposited by groundwater; it was included in the spectrographic analyses for comparison purposes. The sample is massive, medium-grained, yellowish-brown, and contains a number of purple grains in sawed surface which, as in the northwestern Illinois sphalerite, were actually purple bands or growth layers in individual crystals. The purple grains were rather numer-

ous, as in the Dooling sphalerite, but were of a much deeper hue. As the copper content of the Bureau County sphalerite is about twice that of the Dooling sphalerite, it is interesting to speculate that the deeper, more intense color of the purple grains is related to the greater concentration of copper.

A comparison of the other elements shows both similarities and differences between the sphalerites of the two localities, but over-all, the analysis of the Bureau County sphalerite bears a close resemblance to the analyses of the northwestern Illinois sphalerites. The chief differences lie in the ratios of iron to manganese and iron to germanium. However, these variations may indicate only a different source of the mineralizing solutions in the two areas but not necessarily anything about character of source.

Galena.—Spectrographic analyses of galena that was hand-picked under the binocular microscope are shown in Table 2. The first five samples are from crevice deposits in different parts of the district. The last six are from two flat-and-pitch orebodies, the first of which is 3 miles north of Galena, the other 4 miles south of town.

It is difficult to detect any trends of values or any characteristic concentrations of minor elements in specific types of orebodies or geographic locations because of the generally small amounts of such elements. Referring to the last four analyses, which consist of two samples from each of two hand specimens, the erratic values of copper, nickel, iron, and antimony in the same hand specimen suggest that each element is present as inclusions of other minerals rather than incorporated as the element in the galena lattice. Presumably, the inclusions are submicroscopic for the most part, as the only inclusions seen in galena in polished section were marcasite in spaces between cubes, and, strictly speaking, these are not inclusions in the galena but open space fillings in voids. Care was taken to avoid contamination by the marcasite, but some marcasite may have escaped detection.

The even distribution of silver in the two pairs of samples, 23–24 and 25–26, suggests that silver is actually a trace element in the galena. The uniformly low percentage of silver in the samples corroborates earlier reports that the galena of the Upper Mississippi Valley deposits contains negligible silver. On the whole it can be considered galena of an exceptional purity.

Pyrite and Marcasite.—An attempt was made to analyze all the different crystal forms of FeS_2 from every type of occurrence, but the fineness of grain and sparse distribution of some forms and the common admixing of pyrite and marcasite made it impractical to carry out the original scheme. It was decided, however, to analyze the few samples that it had been possible to separate, if only to add to the literature analyses of specific crystal types of FeS_2.

Of the minor elements found (Table 3), cobalt, nickel, molydenum, and arsenic are probably incorporated in the FeS_2 crystal lattice, and copper is probably present as an impurity (11, p. 284). Lead and zinc are also undoubtedly present as contaminants. Too few samples were analyzed to suggest what numerical differences in amounts of elements are important. It would appear, however, that the macrocrystalline varieties contain closely similar amounts, except for the elements present as impurities. The sig-

nificance of the relatively high amounts of cobalt and nickel in the microcrystalline FeS_2 is not readily apparent.

The relative amounts of copper in the various samples may have some significance, even though it may be present as an impurity. Its presence in larger amounts with some varieties of FeS_2 may indicate more favorable conditions for copper deposition at those times, either because of higher copper content of the mineralizing solutions or because conditions for precipitation of the copper from solution were more favorable. Many more samples than were analyzed are needed to evaluate this possibility.

Table 2

Spectrographic Analyses of Galena

Sample No.	Location	Ag %	Cu %	Fe %	Mn %	Ni %	Sb %	Zn %
62	California Diggings, late (C)	.0014	.0005	.002	n.d.	n.d.	.004	n.d.
63	Merry Widow, late (C)	.0010	.003	.001	n.d.	n.d.	n.d.	n.d.
64	Smith no. 1, early (C)	.0004	.0027	.002	n.d.	n.d.	n.d.	n.d.
65	Smith no. 1, late (C)	.0007	.0024	.002	n.d	n.d.	.036	n.d.
66	Appleton, late (C)	.0008	.0026	.002	.001	n.d.	n.d.	n.d.
67	Ginte, late	.0002	.0024	.003	.001	n.d.	n.d.	n.d.
68	Bautsch, early	.0005	.0010	.016	n.d.	n.d.	.002	.002
23	Bautsch, late (1)	.001	.0013	.031	n.d.	.110	*n.d.	*n.d.
24	Bautsch, late (1)	.001	.0004	.110	n.d.	.009	*.0023	*n.d.
25	Bautsch, late (2)	.001	.0002	.018	n.d.	n.d.	.0055	*n.d.
26	Bautsch, late (2)	.001	.0002	.070	n.d.	n.d.	.0123	*n.d.
	Limits of detection	.00002	.0002	.001	.001	.001	.003	.001

(C) = Crevice deposits; others are flat and pitch deposits.

late = post-sphalerite

early = within main sphalerite phase

(1) = Samples 23 and 24 are from different portions of same hand specimen.

(2) = Samples 25 and 26 are from different portions of same hand specimen

* = Limit of detection of Sb is .001% for 23, 24, 25, and 26, which were run at a different time than the other samples.

* = Limit of detection of Zn is .03% for 23, 24, 25, and 26.

Elements not detected and their limits of detection in percent: As (0.01), Ba (0.01), Be (0.0001), Bi (0.0005), B (0.001), Cd (0.005), Cr (0.001), Co (0.001), Ga (0.001), Au (0.004), Li (0.01), Hg (0.2), Mo (0.001), Nb (0.01), P (0.2), Pt (0.01), K (0.1), Na (0.05), Ta (0.05), Tl (0.01), Sn (0.001), Ti (0.001), W (0.01), V (0.001), and Zr (0.005).

Table 3

Spectrographic Analyses of Pyrite and Marcasite

Sample No.	Sample Description	As	Co	Cu	Ge	Mn	Mo	Ni	Pb	Zn
7	Pyrite, octahedral, pre-sl[1] Graham-Snyder (C)	n.d.	n.d.	.0014	n.d.	.001	.003	.002	.019	n.d.
27F	Pyrite, octahedral, pre-sl, Graham-Snyder	n.d.	n.d.	.110	.002	.003	.003	.002	.020	.054
8	Marcasite, coarse tabular, post-sl, Graham-Snyder (C)	n.d.	n.d.	.005	n.d.	.005	.003	.002	.047	.080
13	Marcasite, coarse tabular, pre-sl, Graham-Snyder	n.d.	n.d.	.002	n.d.	.006	.003	.005	.041	.170
15	Marcasite, coarse tabular, post-sl, Bautsch	n.d.	n.d.	.086	n.d.	.0007	n.d.*	.003	.35	.13
16	Same as hand specimen 15	n.d.	n.d.	.031	n.d.	.0008	n.d.*	.006	.44	.36
17	Marcasite, coarse radiating, post-sl, Bautsch	n.d.	n.d.	.0004	.007	.008	n.d.*	.003	.15	2.0
18	Same as hand specimen as 17	n.d.	n.d.	.0006	.007	.013	n.d.*	.004	.28	2.0
9	Marcasite, acicular, post-sl, Graham-Snyder (C)	n.d.	n.d.	.006	n.d.	.012	.003	.002	.024	.090
12(")	Pyrite, cubic, pre-sl, Graham-Snyder	n.d.	n.d.	.004	n.d.	.006	n.d.	.006	.032	.300
10	Pyrite, microcrystalline, Graham-Snyder (C)	0.2	.08	.080	n.d.	.002	n.d.	.061	.14	n.d.
14	Pyrite, microcrystalline, Graham-Snyder	n.d.	.012	.020	n.d.	n.d.	n.d.	.023	.12	.600
	Limit of detection	0.1	.003	.0001	.002	.001	.003	.002	.003	.02

(C) - Crevice deposit; others are flat-and-pitch deposits. The Graham-Snyder (C) samples are from an E-trending crevice deposit overlying but not continuous with the main N. 20 W-trending Graham-Snyder flat-and-pitch deposit.

* - Limit of detection for Mo is .004 for samples 15, 16, 17, and 18. These four samples were run at a different time.

" - Sample sufficient for one trial only. No second observation.

(1) - Sphalerite.

Elements not detected and their limits of detection in percent: Sb (0.01), Ba (0.005), Be (0.0001), Bi (0.005), B (0.003), Cd (0.03), Cr (0.003), Ga (0.01), Au (0.001), In (0.01), Li (0.01), Mg (0.1), Nb (0.02), Pb (0.01), P (0.02), Pt (0.005), K (0.1), Ag (0.0001), Sr (0.02), Ta (0.2), Ti (0.1), Sn (0.003), Ti (0.004), V (0.003), W (0.1), and Zr (0.01).

PARAGENESIS AND MINERAL DISTRIBUTION

The sequence of deposition (Fig. 3) was, in general, pyrite, marcasite, sphalerite, galena, marcasite, and calcite, but variations, overlappings, and repetitions are common. The veins and irregular cavity fillings show the crustification and banding that is characteristic of open space filling (Fig. 5).

Pyrite and Marcasite.—Pyrite and marcasite, as the first sulfides to be deposited, are found throughout the ore-bearing column. Their crystallographic forms in both the flat-and-pitch and crevice deposits are the same. Mineralization began in both types of deposits with pyrite as cubes and cubo-

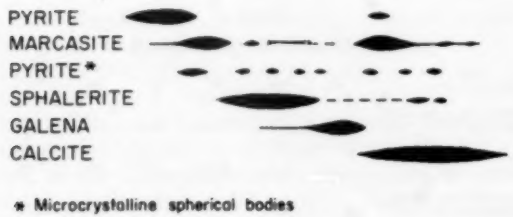

FIG. 3. Sequence of mineral deposition.

octahedrons, impregnating the more vesicular portions of the vein walls and coating the more dense portions. As FeS_2 deposition continued, the pyrite form changed to octahedral, and octahedrons are typical in all deposits as vug linings and as terminations on the pyrite layers along the vein walls.

Marcasite, as a few scattered grains, was deposited with the earliest pyrite of both the deep and shallow deposits and increased gradually during FeS_2 deposition until the marcasite formed, in places, a discrete terminal layer.

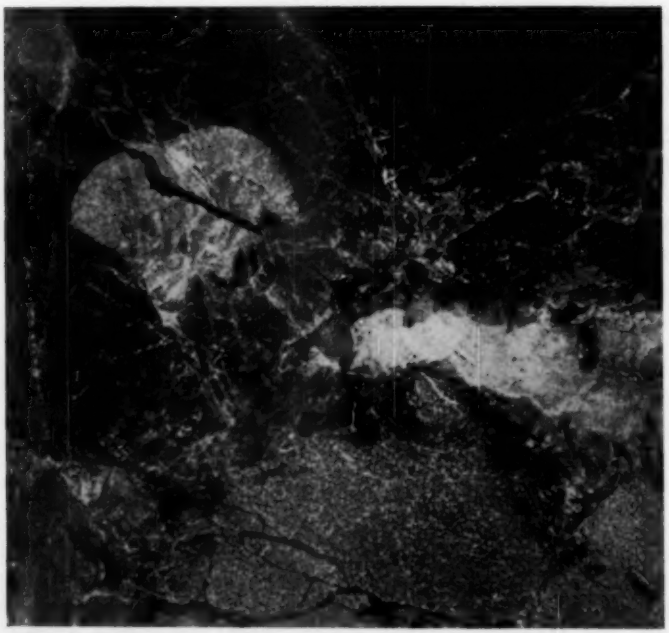

FIG. 4. Polished section of portion of sphalerite vein showing paragenetic relations of globule of microcrystalline pyrite to surrounding sphalerite. Sphalerite is dark, pyrite is speckled gray, calcite is light gray. Pyrite at bottom of photo is next to vein wall. Magnification 5 ×.

The complete sequence from mainly pyrite to all marcasite, however, is found at only a few places. Commonly, in both flat-and-pitch and crevice deposits, some part of the sequence is missing, and at any one place in either type of deposit FeS_2 deposition may have 1) ended prematurely with a mixture of pyrite and marcasite, 2) started late so that the first FeS_2 deposited contained as much as 25 to 30 percent marcasite, or 3) ceased temporarily midway in the FeS_2 stage so that a terminal layer of marcasite lies on FeS_2 which is mainly pyrite. Reversals also are found in that a pyrite-marcasite mixture may be terminated by a layer of pyrite.

Sphalerite.—Sphalerite followed the iron sulfides with only slight corrosion of pyrite and marcasite. It is found in greater abundance in the flat-and-pitch deposits than in the crevice deposits, but its mode of occurrence, its crystal forms, and its paragenetic relations are the same in both types of deposits.

Sheet sphalerite coats the walls of fissures and other more irregular open spaces and exhibits the typical color succession of an early light-colored layer, a middle dark-colored layer, and a late light-colored layer in both flat-and-pitch and crevice deposits.

In the absence of fissures or other open ground suitable for the more massive sphalerite, small radiating or granular aggregates deposited in solution cavities in the dolomite host rock in both deep and shallow deposits. These aggregates in many places show the same color succession as the sheet sphalerite, but in other places they may be entirely light-colored.

The small purple grains, mentioned above, are present in the late light-colored layer on many specimens of both sheet sphalerite and small radiating aggregates. They occur in the sphalerite of both flat-and-pitch and crevice deposits but are not abundant in or characteristic of any specific type occurrence. Their sporadic but widespread occurrence suggests that the special conditions necessary for their formation were found locally in both types of deposits.

Another special event during sphalerite deposition was the formation of the soft, greenish globules of microcrystalline pyrite that were deposited generally at the end of the dark red sphalerite stage in both flat-and-pitch and crevice deposits and that may be related to the concentration of iron in the dark red sphalerite. Figure 4 shows the age relations of these globules to the enclosing sphalerite. The globule is controlled along its lower edge by sphalerite, but its rounded upper side controls the upper pyrite-sphalerite contact. Therefore, the microcrystalline pyrite was deposited on sphalerite and was covered by later sphalerite. The fact that the globules are not abundant in either flat-and-pitch or crevice deposits and yet occur in both emphasizes the sameness of conditions of deposition in both types of deposits.

Galena.—The main part of galena deposition followed the bulk of sphalerite deposition, but galena of an earlier stage is found in places as inclusions in the massive sheet sphalerite. This earlier galena is not important quantitatively but is of common occurrence in both flat-and-pitch and crevice deposits.

The most common type of galena inclusion is an irregular island, ranging

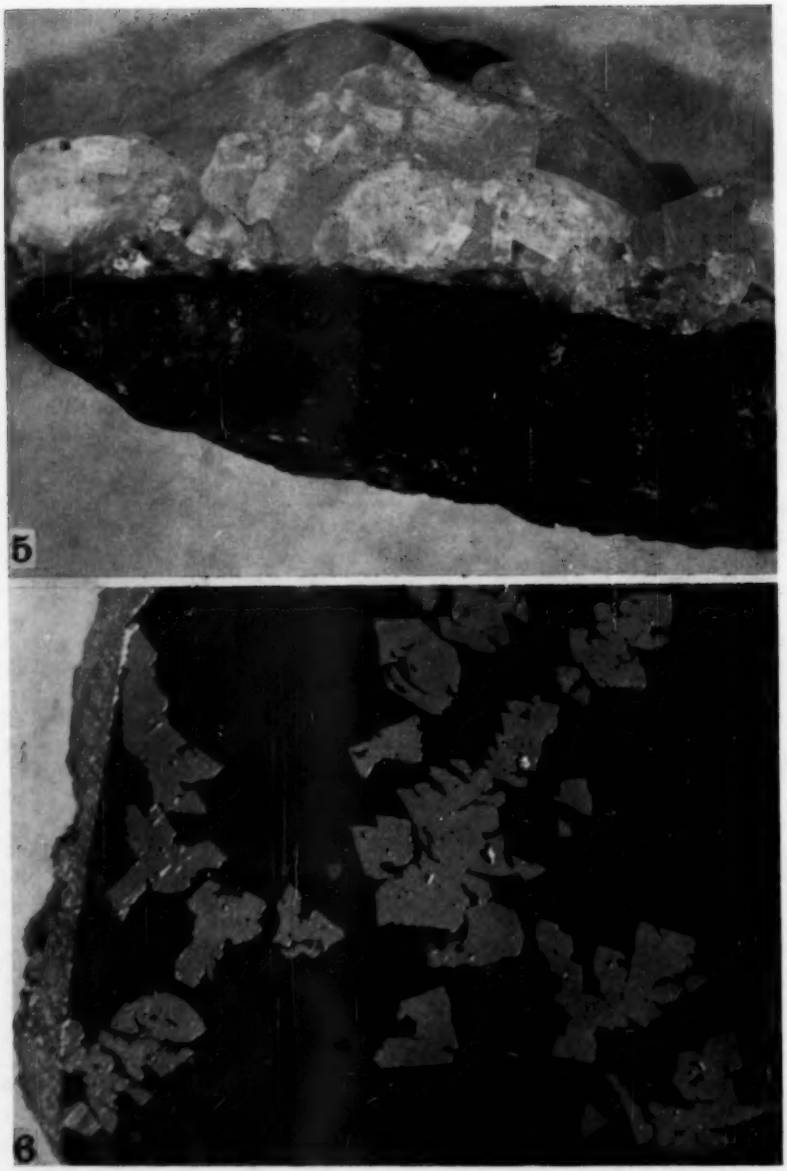

FIG. 5. Typical ore specimen showing crustification and banding characteristic of open-space filling. This specimen represents half of a complete vein and

in size from a tiny speck to about 1 cm in diameter. Another type, elongate arborescent masses (Fig. 6), was found in only three specimens, one from a flat-and-pitch deposit and two from crevice deposits. The arborescent masses parallel the long dimension of the enclosing sphalerite grains and range in width from 0.1 mm to nearly 1 cm and in length from a few millimeters to about 2 cm. Both irregular islands and arborescent masses show an affinity for the dark colored sphalerite and appear to have been deposited along with the enclosing sphalerite. Boundary relations of both types show control by sphalerite faces, control by galena faces, and mutual relations.

The typically massive galena followed sphalerite deposition and is overlapped by it slightly. The overlap is represented by small (1 mm) orange to red-orange sphalerite crystals that were deposited in places along crystal boundaries early in the main galena stage. This orange sphalerite, in contrast to the light yellow, which normally terminates sphalerite deposition, further indicates the affinity of galena for darker colored sphalerite.

Galena was deposited on sphalerite with only a minor amount of corrosion. Extensive replacement of sphalerite was rare, and evidence for it was found on only two specimens.

Galena is characteristically concentrated in the crevice deposits where it may occupy the centers of sphalerite veins or may fill or line fissures or other open spaces without sphalerite. Ordinarily, if sphalerite is a major constituent of a crevice deposit, the bulk of the galena is separated from the major part of the sphalerite. The galena may occur above the sphalerite, on the same level as the sphalerite but separated from it laterally, or, rarely, below the sphalerite.

In the flat-and-pitch structures galena is present to some degree in most deposits but becomes abundant in only a few. Galena is limited to the major horizontal veins (flats) and to the main outside inclined veins (pitches). In many flat-and-pitch deposits galena has been more abundant in the upper parts of the main inclined veins. This has been cited as evidence of vertical zoning within an individual orebody. In other deposits, however, galena has been found to be more abundant in the lower part of the deposit.

The distribution of galena within individual deposits, therefore, does not fit the concept of vertical zoning. The limitation of galena to the major channels and its erratic vertical distribution suggest that galena was deposited in the most easily available open spaces.

Marcasite and Calcite.—The last two minerals to be deposited, marcasite and calcite, are found as coatings on, and veins in, the earlier deposited minerals. Marcasite was the earlier of the two to be deposited, commonly resulting in a layer of marcasite between the earlier sulfides and calcite. Thin layers of marcasite within calcite masses, however, attest to some overlap in the deposition of the two minerals.

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shows, from bottom to top, sphalerite, marcasite (thin layer on sphalerite), and rhombohedral calcite. Fragments of early pyrite layer can be seen at bottom of specimen. Wall rock is missing. Natural size.

FIG. 6. Polished section of ore showing arborescent galena in sphalerite. Magnification 4.5 ×.

From their manner of occurrence and their apparent distribution, calcite and marcasite belong to a later phase of deposition. Their occurrence in veins in the earlier sulfides and as the cement in breccias of the earlier minerals suggests that deposition of calcite and late marcasite followed a period of rock movement resulting from solution and/or diastrophism.

Their distribution, also, suggests a break in the orderly progression of mineral deposition. Whereas the last of the ore minerals, galena, was deposited to a greater extent in the higher strata, the succeeding calcite and late marcasite are more abundant in the flat-and-pitch deposits. This distribution could, of course, merely reflect the extensive weathering of most of the crevice deposits. A few crevice deposits have been observed, however, in which oxidation and weathering were little more than superficial. As calcite and late marcasite were absent from these, it is felt that calcite and late marcasite were never present in as great abundance as in the flat-and-pitch deposits.

Probably following galena deposition there was a period of rock movement during which the mineralized fractures were reopened, allowing the solutions renewed access to the flat-and-pitch structures, with the deposition of calcite and marcasite in the open spaces thus made available. As with sphalerite deposition early in the mineralization period, a plentiful supply of open spaces in the stratigraphically lower structures deterred any abundant mineral deposition in the higher structures.

A possible additional factor in regard to calcite abundance in the lower orebodies is the more calcareous nature of the lower strata. The host rock in most of the 200 to 300-foot ore-bearing section is a dolomite, but the lower 50 feet is variously limestone, calcareous dolomite, and dolomite, with limestone and calcareous dolomite predominating. This factor, however, would have little to do with the increase in marcasite in the flat-and-pitch structures.

POSSIBLE CAUSES OF THE ZONAL ARRANGEMENT OF THE ORES

Mineralogic evidence presented above suggests that conditions of mineral deposition were the same in the crevice deposits as they were in the stratigraphically lower flat-and-pitch deposits.

The two classes of deposits do not represent zones as conceived in the classic zonal theory, that is, zones of differing conditions of deposition. The occurrence of the same minerals with identical habit, color, and even minor element content in both types of deposits indicates that there was essentially no change in conditions of deposition from the deep flat-and-pitch deposits to the shallow crevice deposits. Nevertheless, the fact remains that there is a marked increase in the ratio of galena to sphalerite from deep to shallow deposits. There is, in fact, a zonal arrangement of the ores, whatever the underlying cause may have been.

One way of obtaining this type of zonal arrangement is suggested by the spatial relations of sphalerite and galena within individual orebodies. These relations indicate that within any one orebody the location of open spaces controlled the distribution of sphalerite and galena. Such control

depends upon time and sequence of deposition, with the earlier deposited minerals filling or sealing off certain open spaces and the later minerals being deposited in the spaces that remained.

If such a concept is projected from individual orebodies to the whole district, the zonal arrangement represents a "time-zoning." The earlier solutions deposited sphalerite in the deeper structures, but also to some extent in the shallower structures. By the time galena deposition began, most of the open spaces in the deeper flat-and-pitch structures were filled or sealed off, and the shallower crevices offered the most convenient open spaces.

The basic control in such a scheme is the composition of the mineralizing solutions. If the only control at the site of deposition is the location of open spaces, then the solutions must change with time. They must be, initially, iron-bearing, changing to zinc-bearing and, finally, to lead-bearing, with a resurgence of iron from time to time.

An alternative explanation for the vertical change in the ratio of sphalerite to galena involves changes in conditions at the site of deposition rather than compositional changes in the mineralizing solutions. Several investigations bearing on the problem of mineral deposition in the Illinois-Wisconsin district offer some measure of support to this alternate hypothesis.

The work of Newhouse (10) and Garrels (5) suggested that a high chloride ion concentration in the mineralizing solutions was responsible for the late deposition of galena. On the basis of Garrels' investigations, Behre and Garrels (2) proposed that the cause of precipitation was mingling of the mineralizing solutions with groundwater. Neutralization by bicarbonate ions in the groundwater, aided by reaction with the carbonate wall rock, was postulated as the cause of the precipitation of zinc sulfide. Lead, complexed and held in solution by a high concentration of chloride ions, was said to have been precipitated later by dilution of the chloride ion concentration.

The cooling effect of the groundwater probably also played a part in the localization of the deposits. Garrels (5) showed that the effect of chloride ion on lead solubility is increased with increasing temperature. Thus, the cooling effect alone would create conditions favorable for galena deposition. That cooling did take place during mineral deposition has been shown by Bailey and Cameron (1). Working with fluid inclusions in sphalerite and, to some extent, calcite, they found that mineralization took place on a decreasing temperature scale.

Following the proposal of Behre and Garrels (2), it is possible to integrate the results of the mineralogic study presented in this paper with the investigations of Newhouse (10), Garrels (5), and Bailey and Cameron (1). The mineralogic evidence indicates that individual mineral species were deposited under conditions that were the same in both crevice and flat-and-pitch deposits. On the other hand, fluid inclusion temperature data suggest that the different mineral species may have been deposited under different conditions. Assuming that dilution and cooling by groundwater were the chief causes of precipitation, the two somewhat conflicting lines of evidence can be reconciled by a gradual lowering of the zone of groundwater with time. The conditions favorable for galena deposition (greater dilution and cooling

of the mineralizing solutions) will then encroach on the lower sphalerite zone, resulting in deposition of galena where sphalerite previously had been deposited. The distribution of galena within a deposit would still depend on the location of available open spaces, as with the theory of mineral deposition by solutions of changing composition.

There is little direct evidence in favor of one theory over the other. The distribution of the minerals and their relations to one another can be explained equally well by either theory. However, when the less direct evidence from the researches of Newhouse (10), Garrels (5), and Bailey and Cameron (1) are considered, the second theory, involving changing conditions of deposition, seems the more probable.

ILLINOIS STATE GEOLOGICAL SURVEY,
URBANA, ILL.,
April 27, 1960

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THE ROLE OF REPLACEMENT IN THE ORIGIN OF SOME COCKADE TEXTURES

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ABSTRACT

The authors present evidence that cockade textures are not in all cases formed according to the hitherto accepted view, i.e. by successive deposition of minerals around rock fragments or fragments of vein filling. Three cases of cockade textures from Czechoslovak localities are described, in which layers forming fringes around rock fragments are younger than the mineral cementing them.

In the first of the three described cases, rock fragments are fringed by quartz and tetrahedrite (Polkanová, Slovakia), in the second case by quartz alone (Gelnica, Slovakia) and in the third case by sphalerite and quartz (Příbram, Bohemia). In all these cases the remaining space between the rock fragments is filled by siderite that originally represented the only cementing component. Later it was replaced by the above components in the direction away from the boundary with the rock fragments, giving rise to lining layers and thus to a texture called cockade. During the origin of the quartz band, a marked replacement of outer parts of the rock fragments also took place (especially in Polkanová and Gelnica).

In view of these results it is desirable to revise the existing descriptions of cockade textures in the literature. It cannot be excluded that some of them may have been formed analogously as the textures described from Polkanová, Gelnica and Příbram.

The present paper should at the same time contribute to the mechanism of formation of the so-called "segmented veinlets," known under this name from mineragraphic literature, as well as to the investigation of quartz metacrysts in siderite.

PRINCIPAL EXISTING VIEWS ON THE ORIGIN OF BRECCIA AND COCKADE TEXTURES [1]

THE term cockade or ring texture applies in geological literature to rock fragments or fragments of older components surrounded in space (or lined when observed in a plane section) by a layer or layers of one or several minerals and in which the remaining space between the surrounded (lined) fragments is filled by another component (or components).

If the older fragments are not lined by any layers and the interspaces are filled by a single mineral (or by several minerals without any marked lining of the older fragments) it represents a mere breccia texture.

Since the presence of older fragments is necessary for the formation of cockade textures the discussion relevant to the origin of cockade textures is closely connected with the problem of origin of breccia textures.

[1] In common with H. Schneiderhöhn (1941) and G. M. Schwartz (1951) "texture" is preferred to "structure" in connection with breccias and cockades.

Fragments of rock or other material are generally not in mutual contact in a plane section. This gave rise to various explanations of the origin of breccia textures, some of which are cited by R. Beck (4) as early as 1901 (p. 201–203) and 1903 (p. 193–195) and which are reviewed in the paper of S. B. Talmage (20). Following are the principal concepts published in the literature, including the more recent papers available:

1. The common lack of contact in a plane section is caused by the fact that the fragments were originally floating in the medium from which the vein was formed (some authors speak generally of a fluidum, others directly about a strongly viscous gel). To this possibility it should be added that the heavier fragments could sink in the gel and—unless they were isolated—should touch, whereas the lighter fragments could be floating in it and may now appear unsupported.

2. The fragments touch mutually in space and the position of the section will determine whether the contact will be observed or not.

3. The fragments were formerly in touch but were separated and isolated due to crystallization of vein components.

4. The fragments are interpreted as xenoliths imported by the injected solution that gave rise to the vein and probably was rather concentrated (8).

5. We are not dealing with fragments but with relicts after replacement. It should be noted in this connection that the angularity itself of inclusions does not eliminate the possibility that we are dealing with replacement relicts as shown by A. M. Bateman (3).

From a theoretical point of view, however, not all possibilities of formation of breccia textures are thereby exhausted. Particularly the following should be added:

6. The falling of fragments could take place during the period of deposition of a mineral. The shape of its solid, already deposited layer, as well as the width of the remaining free space in the fissure, and other factors, could cause the fragment to be trapped and gradually to be surrounded by the depositing mineral. A part of the material of the surrounding mineral was thus deposited earlier and a part later than the trapping of the fallen fragment took place. If several fragments fell simultaneously they would be in contact; if, however, they fell only here and there they could be totally surrounded by the depositing mineral and lack any mutual contact, without the necessity of advocating the phenomenon of floating in a gel medium. This case corresponds fundamentally to a note made by S. B. Talmage (20, p. 608).

It follows from the above that in order to understand properly the origin of a given breccia texture a detailed genetic investigation of the vein at the given place must be undertaken and that it is insufficient merely to determine whether the fragments touch in space or not. In spite of this, however, such a determination is very desirable in connection with the investigation of origin of breccia textures. As early as 1893 the problem was taken up by F. Pošepný (14). In his classical work of 1893 (p. 64–65) he maintains that he always found contact of fragments when he sliced a specimen into plates, where the fragments were not in contact on the specimen surface.

S. B. Talmage (20) used a synthetic plastic to imitate breccia textures and then he cut them. He showed very clearly that in the case of irregular fragments placed one above the other their contacts in a plane section are usually of point character and very uncommon. The isolated character of fragments in sections is rather regular than exceptional. Occasionally, their contact cannot be observed at all in a plane section and still they are in mutual contact in space.

As far as cockade textures themselves are concerned their origin was explained (in all papers available) by successive deposition of minerals around earlier fragments. The most detailed description and graphical representation of such a process was presented by J. E. Spurr (18) who used cockade textures from the Alacrán Mine in Zacualpan, Mexico. Some authors are of the opinion that the fragments, around which successive layers were formed, were floating freely in the medium that gave rise to the layers. They do not mention, however, how they verified the isolated character of the fragments (18; 5, p. 343 and Fig 318, p. 96–98 and Figs. 60, 61). Other authors either directly express their view that the fragments touch in space within the cockade texture under investigation (14, p. 64–65; 11, p. 299–300 and Figs. 41 and 42), or they are inclined to share such a view (2, p. 17; 16, p. 103, and others). Finally some authors do not consider this problem but explain the origin of the layers on the basis of successive deposition in the direction away from the boundaries of rock or other fragments (21, p. 100 and Figs. 63 and 64; 17, p. 582; 7, p. 19; 19, p. 26–27 and Figs. 23 and 24; 5, p. 54, Fig. 24, and others).

H. Schneiderhöhn (15, p. 268–9) admits of the existence of both cases in hydrothermal deposits. He thinks that textures with fragments in contact are perhaps more abundant but that in many cases of cockade textures there were unsupported inclusions in which angular or rounded fragments of the surrounding rock were totally surrounded by layers of ore and other components. As far as the origin of cockade textures is concerned he does not exclude the theoretical possibility of fragments floating in a viscous gel medium prior to its crystallization, but he considers such a case only very rare, if at all possible.

In the present paper it is not intended to exclude *a priori* any of the six explanations of the origin of breccia textures, mentioned at the outset, or to maintain the natural occurrence of all these possibilities.

The possibility of the second explanation, however, was demonstrated by Pošepný (14) and successfully imitated experimentally by Talmage (20); it certainly is not exceptional under natural conditions. It was shown by our investigation that when the fragments are or were originally in mutual contact, their boundaries with the mineral filling the space between them could have served as import routes for younger solutions. From these solutions, layers lining the fragments were formed metasomatically, giving rise to the cockade texture. Reasons are presented why some of these lined fragments need not be in spatial contact.

The described process of formation is not generalized for all cockade

textures but it is shown that it plays an important role in the origin of some of them.

COCKADE TEXTURES FROM POLKANOVÁ NEAR BANSKÁ BYSTRICA, SLOVAKIA

The investigated material comes from the vein Hrča I in Polkanová, in the mining district of Staré Hory—Špania Dolina,[4] north of Banská Bystrica in Slovakia, which was famous in Central Europe especially in the first half of the 16th century for its copper and silver ore mining.[5]

The ore deposits of the district were described in detail by Koutek (9, 10). The vein Hrča I, from which the cockade textures originate belongs according to Koutek (9) to ore-bed veins, which, together with true veins, occur in the local "sub-Tatric crystalline series" and verrucano. The vein Hrča I is according to Koutek embedded in gneisses that are sericitized in its vicinity. Koutek (9) also gives a brief description of the local cockade textures.

The authors are indebted to Professor Koutek for the stimulus to carry out a microscopic revision of cockade textures and for supplying material for investigation.

We had six samples at our disposal, all of them displaying on their surface sections angular to rounded fragments (Fig. 1) formed by sericitized rock, incrusted with quartz. Only one of the fragments was larger than 10 cm, the others being considerably smaller. During the time of incrustation with quartz a light zone with predominant quartz was commonly formed in the marginal part of the fragments, which may often be observed even macroscopically (e.g. the large round fragment in the upper right-hand part of Fig. 1). Particularly in small-size fragments the incrustation sometimes proceeded as far as their center so that without recognizing this process they could be interpreted as rounded fragments of some older quartz (e.g. the small fragment in the lower left-hand corner of Fig. 1, right of the large pointed one).

At some places, it was possible to observe immediate contact of quartz-incrusted fragments, or a contact through their marginal quartz zone (if it was developed), on the surface of the specimens as well as during the crushing one of them. Otherwise, in agreement with the general conclusion of Talmage (20) the fragments mostly did not touch in the plane section.

On examining the large round piece of rock in the right-hand corner of Figure 1, the quartz fringe of which was formed partly by replacement of its outer zone, it may be seen that such a process may generally result in some formerly mutually touching fragments not now with mutual spatial contact.

The shape of the layers may be seen on polished samples (Figs. 2, 3). Quartz fringes have different thickness on different fragments (Fig. 2); where a marked silicification proceeded to the center of the fragment, the

[4] The Spania Dolina locality (German Herrengrund, Hungarian Urvölgy) is well known to mineralogists as the original locality of "herrengrundite" ("urvölgite"), which was found by Meixner in 1940 to be identical with devillite, $CaCu_4[(OH)_8|SO_4]_2 \cdot 3H_2O$.

[5] The principal primary ore minerals here are a silver-containing antimony tetrahedrite and chalcopyrite.

quartz fringe is generally not present (Fig. 3). Tetrahedrite fringes around fragments are also commonly of different thickness (cf. Figs. 2 and 3) and this thickness may vary considerably even around a single rock fragment (Fig. 2).

A typical feature is represented by the veinlet-like projection of tetrahedrite into the surrounding siderite (Fig. 2), and by the connection of tetrahedrite fringes belonging to two close-lying fragments (Fig. 3). At such places, a large accumulation of tetrahedrite substance between rock fragments takes place. These macroscopic observations alone indicate that

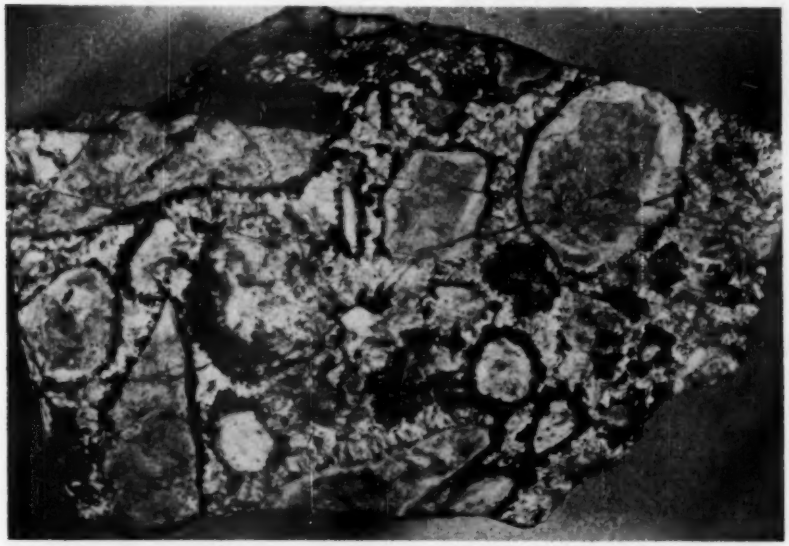
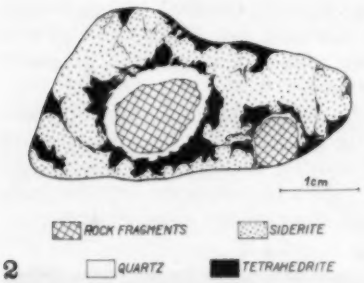


FIG. 1. Cockade texture from Polkanová (Czechoslovakia) with fringes of metasomatic origin, younger than the siderite cement between rock fragments. White, quartz; black, tetrahedrite. Natural size 18 × 10 cm.

tetrahedrite is younger than siderite and that therefore in this case the cockade texture could not have been formed by successive deposition of minerals about older fragments as has been hitherto described in the literature.

Microscopic examination of polished sections shows that tetrahedrite fringes are generally not continuous and commonly send out projections in the form of metasomatic veinlets into surrounding siderite. Under crossed nicols it may be seen that tetrahedrite veinlets very clearly follow boundaries of siderite grains (Fig. 4) or else cut across the grains irrespective of their boundaries (some of the veinlets in Fig. 5).

Figure 5 shows a quartz zone and a discontinuous tetrahedrite fringe with the adjacent part of the rock fragment on one side and with the siderite



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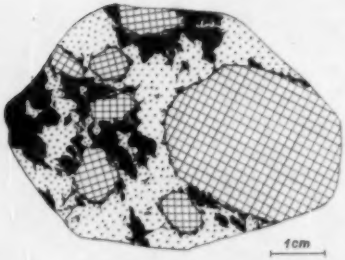

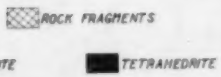

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FIG. 2. General view of a polished section of a cockade texture from Polkanová displaying the irregular thickness of the tetrahedrite zone and its penetration, through numerous extensions and metasomatic veinlets, into surrounding siderite.

FIG. 3. General view of another polished section of a cockade texture from Polkanová displaying differences in thickness of the tetrahedrite zone when comparing different fragments and showing a typical accumulation of tetrahedrite in the region between close-lying rock fragments.

FIG. 4.[13] Replacement of siderite by tetrahedrite and quartz along the boundaries of differently oriented siderite grains, Polkanová.

mass on the other side, in other words, a section of a cockade texture such as in Figure 2.

The quartz zone of Figure 5 contains a considerable amount of siderite inclusions representing the relicts after its replacement by quartz. An example of their shape, abundance and distribution is given by Figure 6, which is an enlarged part of the quartz zone of Figure 5.

The entire quartz zone, however, was formed not only by replacement of the siderite mass bordering on the rock fragment, but also partly by re-

[13] Figure 4, in common with all other hand-drawn details of microscopic observation of polished sections, was prepared by projecting the object under observation by arc light at partially crossed nicols, using a horizontal microscope (Neophot, made by C. Zeiss) with a projecting mirror.

placement of the fragment itself. This is evidenced by minute rock relicts enclosed in that part of the quartz zone adjacent to it. In addition, quartz penetrates by numerous projections and other metasomatic forms into the rock fragment so that their boundary is very complex. In Figure 5, in order to make it quite clear where the rock fragment actually begins, its boundary with the quartz zone was simplified. As the rock fragment was penetrated by siderite prior to the replacement by SiO_2 it is not surprising to find siderite

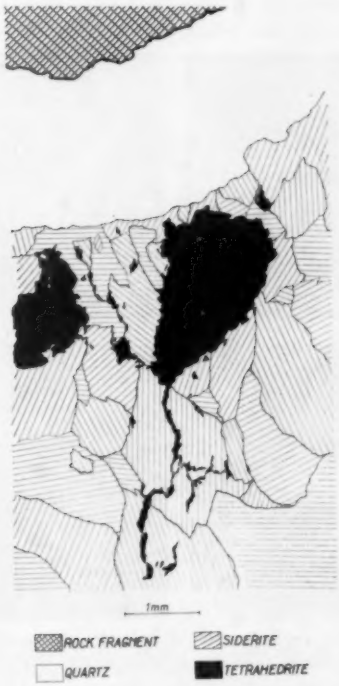


FIG. 5. Part of a cockade texture from Polkanová as seen in Figure 2. Siderite is replaced by tetrahedrite in the direction away from the quartz zone, the tetrahedrite partly following the boundaries of differently oriented siderite grains, partly cutting across them.

relicts in the adjacent part of the quartz zone, in addition to rock fragment relicts.

Quartz and tetrahedrite forming fringes around rock fragments penetrate abundantly into the main siderite mass in the space between the fringed fragments. If tetrahedrite and quartz are developed in the form of veinlets they commonly have a segmented character similarly to the "segmented veinlets" described by Bastin (1, 2) from South Lorraine, Ontario. Unlike

the cases described by Bastin, the "segmented veinlets" found here do not represent rupture fillings, but veinlets formed by replacement.

The segmented character of veinlets from Polkanová may be caused by a single exchange of quartz for tetrahedrite in the course of the veinlet (upper right-hand part of Fig. 4 and Fig. 8), in places by its two- or several-fold repetition (Fig. 10). The mechanism of formation of these segmented veinlets was taken up in more detail with special reference to the problem of whether both components constituting them are contemporary or of different age.

It is important in the first place that both tetrahedrite and quartz commonly form independent metasomatic masses as seen in polished sections, the

FIG. 6. Relicts after replacement of siderite by quartz. Part of the quartz zone from Figure 5 selected so as to contain more abundantly preserved siderite relicts. Polkanová.

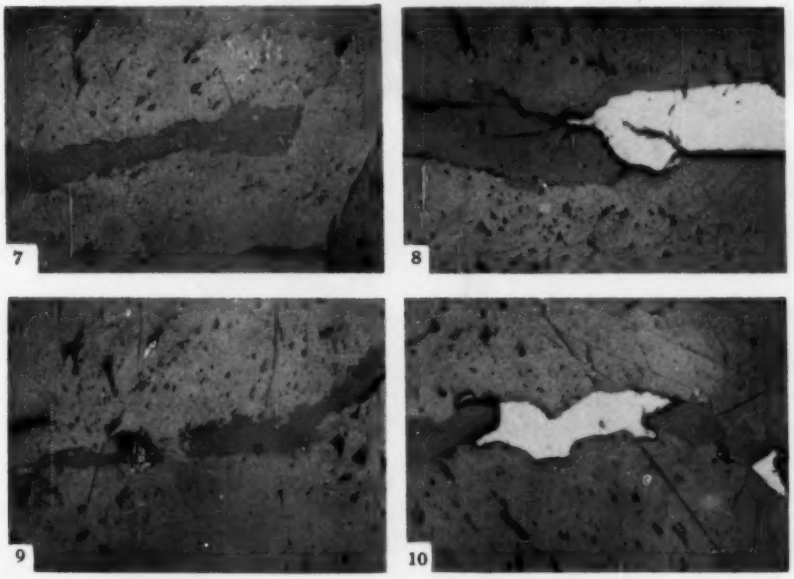
masses sending out metasomatic veinlets into their vicinity (Fig. 11). The encounter of quartz and tetrahedrite giving rise to a simple segmented veinlet in the area between such independent accumulations of quartz and tetrahedrite indicates that both minerals were formed here (Fig. 11) independently of each other on a suitable channelway that was in places represented by cleavage planes, or else perhaps by minute cracks, but commonly by grain boundaries (Fig. 4).

In the upper right-hand part of Figure 12 a segmented veinlet of quartz-tetrahedrite may be seen as a continuation of a typical quartz metacryst,[6]

[6] The term metacryst is used here to denote crystals formed by replacement of an older component and outlined more or less idiomorphically with respect to it, the term being due

enclosing smaller relicts of unreplaced siderite. It might appear at first sight that tetrahedrite and quartz are of the same age in this veinlet, but it is indicated by the remaining tetrahedrite mass, on account of its location along the idiomorphically bounded side of the quartz metacryst that tetrahedrite is younger than quartz.

This figure reminds one of the photomicrograph of a polished section from the Tetyukhe deposit in the USSR appearing in the paper by Genkin (5, p. 207, Fig. 185) where the continuity of an idiomorphically bounded, imperfect crystal of arsenopyrite with an arsenopyrite-ilvaite veinlet representing basi-



FIGS. 7 to 10. Details to the origin of quartz-tetrahedrite segmented veinlets formed during the replacement of siderite. Further explanation in the text. Light gray, siderite; dark gray, quartz; white, tetrahedrite. Magn. 85 ×.

cally a crack filling in chalcopyrite, served as a criterion for the conclusion that it is an arsenopyrite metacryst in older chalcopyrite.

Figure 13 shows another criterion for the determination of the relative age of quartz and tetrahedrite. Tetrahedrite, which is evidently younger than siderite (Figs. 4, 5, 11 and others), replaces in Figure 13 siderite from its boundary with quartz, giving rise to a "fossil boundary" in the sense of Kutina (12). It is worth while to compare in this figure the shape of the boundaries between quartz and tetrahedrite at those places where siderite

to Lane (1903) and used by Lindgren (13), Schneiderhöhn (15), Betekhtin and Genkin (5) and others. The terms xenoblast and idioblast shall not be used.

was replaced (A′ and B′) with the similar course of boundaries at those places where siderite was not replaced (A and B).

The above-established succession siderite-quartz-tetrahedrite should be applied to interpret the origin of segmented quartz-tetrahedrite veinlets.

Quartz and tetrahedrite veinlets, as long as they are monomineral,[7] are commonly discontinuous (Figs. 9, 14). In the case of a discontinuous tetrahedrite veinlet (Fig. 14) no later filling of spaces between the tetra-

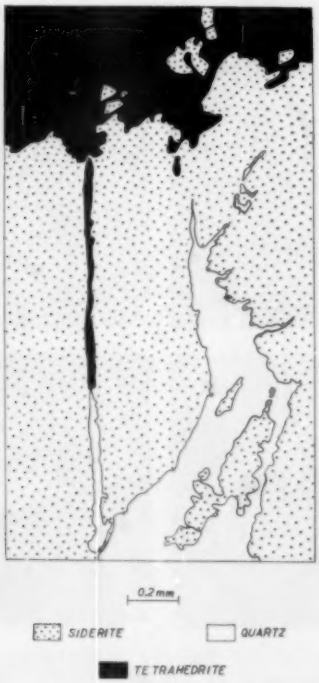


FIG. 11. The existence of independent metasomatic forms of quartz and tetrahedrite, with extensions issuing into their vicinity indicates that the components of the quartz-tetrahedrite veinlet in the region between the quartz and the tetrahedrite mass are not of the same age. Polkanová.

hedrite segments by quartz could take place, quartz being older than tetrahedrite. In the opposite case, with a discontinuous quartz veinlet (Fig. 9) spaces could have been filled by tetrahedrite, giving rise to a segmented veinlet (Fig. 10) if ore material was imported to such places.

If an import of ore solutions took place at the termination of a quartz veinlet only a simple continuation of a tetrahedrite veinlet on a quartz one was brought about. At places where the termination of the quartz veinlet

[7] Or in that part of their course where they are monomineral.

was more or less straight (Fig. 7) there existed conditions for the formation of a segmented veinlet with a straight contact between the two minerals (Fig. 8). Rectilinear bounding of quartz in a veinlet is occasionally clearly caused by the tendency of quartz to be idiomorphic in siderite (cf. the left-

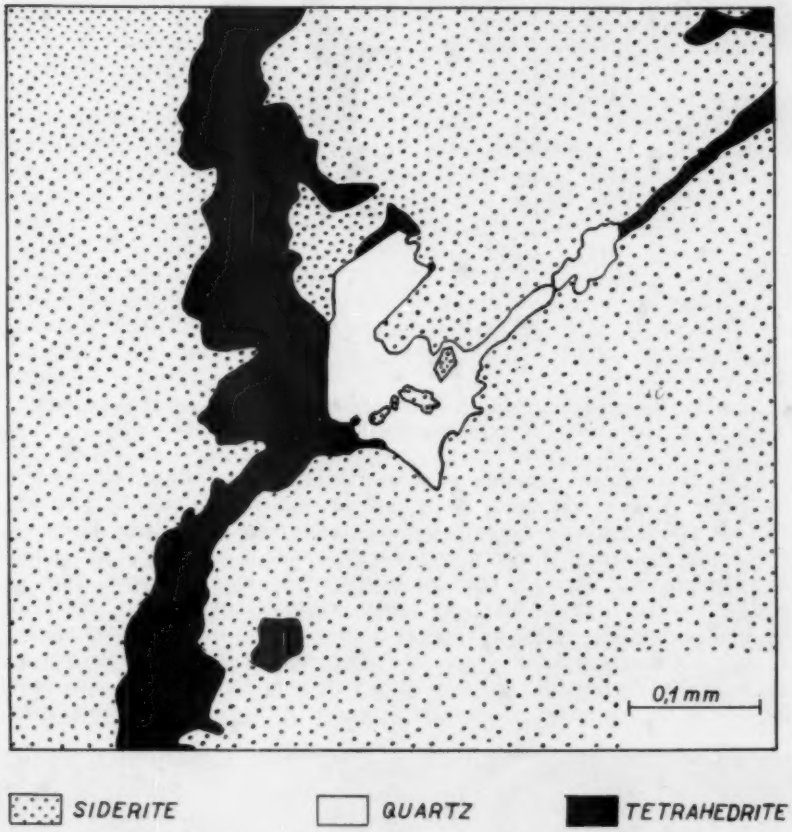


FIG. 12. An incomplete metacryst of quartz with siderite remnants developing from a quartz-tetrahedrite veinlet. The shape and distribution of tetrahedrite around the idiomorphically bounded quartz face bring up the possibility that the tetrahedrite in the adjacent veinlet can also be younger than quartz. Polkanová.

hand part of Fig. 10, the contact of quartz with tetrahedrite), in places perhaps by other reasons (Fig. 7).

At those places where the quartz veinlet becomes narrow and wedged out the contact with tetrahedrite is commonly only of point character (Fig. 11) or no direct contact can be observed in a plane section (Fig. 14).

FIG. 13. Replacement of siderite by tetrahedrite away from the boundary with quartz. More details in the text. Polkanová.

The discontinuity, whether of a quartz or of a tetrahedrite veinlet in the plane of some sections is easily understood. Let us imagine a veinlet that has basically a tabular form in space. If the plane of the polished section cuts across the marginal part of such a body, where it becomes narrower and is irregularly and unevenly bounded in space [8] it may be expected that the polished section will disclose only cross-sections of its farthest projecting marginal extensions, which will appear in the plane as an interrupted veinlet. If such a plane is polished deeper and deeper either a gradual merging of the individual "segments" will take place until they form a continuous veinlet, or else the segments will decrease in size until they disappear completely,

FIG. 14. An interrupted tetrahedrite-quartz veinlet in siderite. More details in the text. Polkanová, Magn. 60 ×.

[8] Not to mention its irregular lateral bounding, so typical of numerous metasomatic veinlets. It should be added to the concept of the tabular shape of the veinlet used here for clarity only, that such a shape is characteristic especially for crack fillings whereas metasomatic veinlets often deviate from this shape very considerably.

depending on the side from which the polished section was prepared with respect to the tabular body. Figure 14 shows an example where gradual grinding of a polished section resulted in the disappearance of the tetrahedrite veinlet segments (particularly of the segment in the center of Figure 14, lying closest to the quartz veinlet) and in the increase of distances between the segments. This indicates that by polishing the sample we approached the end of the unevenly bounded metasomatic body manifesting itself as a veinlet in the plane section.

In a few cases, carbonate, either ankerite or dolomite, was found in segmented veinlets together with tetrahedrite and quartz.[9] The possibility of the origin of tetrahedrite segments by previous replacement of ankerite was eliminated by the finding of siderite replacement relicts in the tetrahedrite segment, immediately adjacent to the ankerite segment, as well as by the shape of the boundary between tetrahedrite and ankerite, which did not suggest the replacement of ankerite by tetrahedrite.[10] The possibility of formation of tetrahedrite segments by replacement of parts of a quartz veinlet was eliminated by the finding of selective replacement of siderite by tetrahedrite from the boundary of siderite with quartz (see above).

In conclusion, let us summarize briefly the origin of cockade textures from Polkanová:

Spaces between crushed rock formed by mutually supported fragments of mostly sericitic gneisses were penetrated by solutions that deposited siderite, which mostly filled the spaces completely. Only a few little cavities were left. During this process the rock fragments themselves were also impregnated by siderite. A further ascent of solutions proceeded along the boundaries of the rock fragments with the siderite cementing them. They deposited quartz, which caused a quartz-incrustation of the fragments and gave rise to a quartz zone around them (partly by replacing the surrounding siderite, partly by replacing the adjacent marginal parts of the fragments themselves). In addition to this, quartz penetrated commonly into the main siderite mass in the direction away from the boundaries with rock fragments, giving rise to various metasomatic forms, particularly veinlets, following up preferentially the boundaries of differently oriented grains and cleavage planes of siderite.

Subsequent solutions now depositing tetrahedrite ascended along the quartz-siderite boundaries since the boundary of rock fragments with quartz became less convenient as an import route on account of metasomatic projection of quartz into rock fragments and due to a much higher solubility of siderite under the given conditions. Ore solutions replaced siderite selectively away from its boundaries with quartz, giving rise to a more or less continuous zone following the quartz zone around the rock fragments.

[9] Koutek (9) reports ankerite from the locality in question. In the following, our carbonate shall be provisionally considered also as ankerite.

[10] Ankerite can be easily distinguished in the polished section from siderite by the lower reflectivity of the former and by positive one-minute etching with HCl 1 : 1. Calcite was excluded by the practically negative response to 6% acetic acid (etched for 1 min.). For the sake of comparison, etching was carried out simultaneously on guaranteed ankerites and calcites from other localities.

Tetrahedrite also frequently penetrated into the main mass of siderite giving rise to metasomatic veinlets commonly following quite clearly the boundaries of siderite grains. During this process, quartz and tetrahedrite also penetrated at some places successively into some small cavities in siderite.

Such was the process of formation of cockade textures in Polkanová where siderite was the only original cementing material of rock fragments.

COCKADE TEXTURE FROM GELNICA IN SLOVAKIA

Our attention was attracted by a specimen possessing cockade texture that belongs to the collection of the Department of Mineral Deposits of the Charles University in Prague; the specimen came from Gelnica in Slovakia and has the approximate size of $10 \times 7 \times 5$ cm. It consists of rock fragments formed by sericitic phyllite rich in quartz, and secondarily incrusted

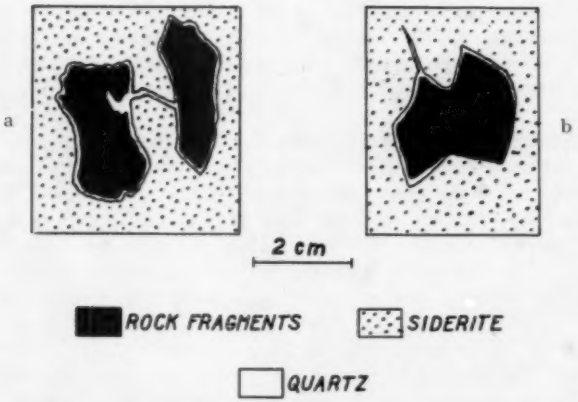


FIG. 15. Macroscopic criteria indicating that quartz fringes around rock fragments can be younger than siderite cementing these fragments. A cockade texture from Gelnica.

with it, which are bordered by a narrow quartz zone, the spaces between them being filled with siderite. In an independent quartz mass present in a part of the specimen some chalcopyrite could be detected.

The quartz fringes around rock fragments have mostly a constant thickness but at one place projections of quartz into surrounding siderite could be observed macroscopically (Fig. 15b); at another place a quartz veinlet connecting quartz fringes of two close-lying fragments could be seen (Fig. 15a). In places of greater accumulation of small rock fragments a greater concentration of quartz took place so that in a few places several rock fragments were jointly surrounded by it, whereafter it extended about some of them.

From such places a part of the specimen was separated in order to prepare a polished section (Fig. 16). Macroscopically, by examining with a lens,

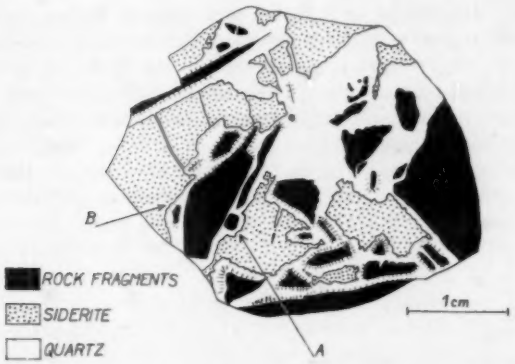


FIG. 16. General view of a polished section prepared from a fragment of vein filling from Gelnica, which possessed cockade texture. The picture shows the replacement of siderite and of rock fragments by quartz.

the growth of crystal individuals of quartz in the direction away from the rock fragments is well apparent. In the left-hand part of the picture, the connection of the quartz fringe of the large fragment with that of the narrow long fragment through three veinlets is very marked, the veinlets running

FIG. 17. Detail of the place marked A in Figure 16. Quartz replaces a rock fragment on the one hand, and siderite along the boundaries of its differently oriented grains on the other hand. The width of the quartz zone is about twice reduced. Gelnica.

approximately parallel to each other and cutting across siderite. In the upper part of the picture a more extensive replacement of siderite may also be observed, its large relicts being preserved, the distribution of which indicates their original connection. In the upper right-hand part of Figure 16 are relicts remaining after the replacement of rock material, in the region of a large accumulation of quartz.

In analogy with such places it may easily be imagined that the replacement of the outer part of the fragments could here and there result in a

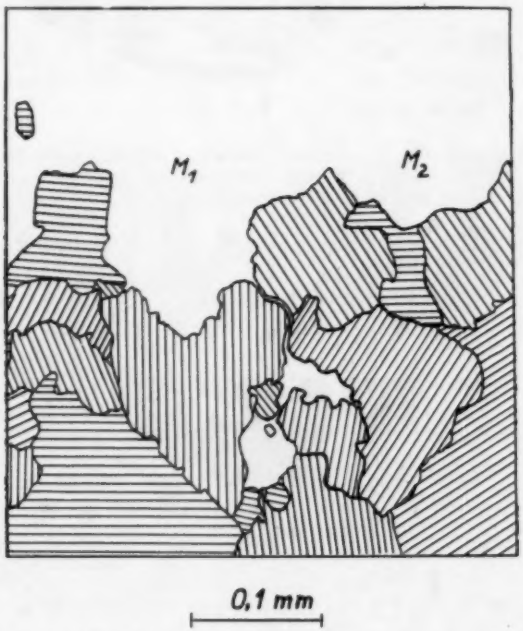


FIG. 18. Detail of the place marked B in Figure 16. An example of termination of quartz individuals growing in the direction away from the rock fragment into surrounding siderite. The picture shows an unevenly bounded metacryst (M_1), continuing in the form of a thin veinlet along the boundaries of siderite grains, the veinlet developing further into two irregularly bounded metasomatic forms. Gelnica.

spatial isolation of their relicts originally belonging to fragments, which were mutually in contact. Thus it is possible that some fragments in the lower part of Figure 16 are not in contact at present due to such a replacement process. On the other hand, it is probable that the rock relicts appearing in the upper right-hand part of the figure represent relicts after replacement of one and the same rock fragment. The fact that the texture examined was formed basically from a true breccia texture is evidenced by different orien-

tation of the schistosity of some cockade-lined fragments as may be seen on observing macroscopically the sample from which the polished section had been prepared.

Figure 17 shows a microscopic detail of a polished section from a place marked A in Figure 16. In the upper part of Figure 17, metasomatic penetration of SiO_2 into the rock fragment may be observed and in the lower part of the same figure siderite is markedly replaced by quartz along the boundaries of differently oriented grains. In the lower left-hand part of Figure 17, several relicts are oriented identically after siderite replacement, which may be taken as an indication of their being originally connected.

Figure 18 is a microscopic view of the termination of quartz individuals projecting into siderite at the place marked B in Figure 16. The continuation of the quartz crystal (M_1) in the narrow veinlet running along the boundaries of siderite grains and its lobar extension along the boundaries of other grains (Fig. 18) represents a criterion demonstrating that the quartz individuals more or less perfectly crystallographically terminated, were also formed by replacement of siderite, in other words, that we are dealing with metacrysts.

The above-mentioned macroscopic as well as microscopic observations prove that the cockade texture from Gelnica was formed in a similar manner as the cockade textures from Polkanová: Solutions depositing quartz ascended along the boundaries of rock fragments with siderite (which was originally their only cementing component) and partially replaced siderite, partially rock fragments, giving rise to the layers and to a cockade texture.

COCKADE TEXTURE FROM THE ŠEVČÍN VEIN IN PŘÍBRAM

The third case that aroused suspicion that the cockade texture in question may not have been formed according to the hitherto accepted explanation, is a fine specimen obtained some years ago by one of the authors (J. K.) from J. Bambas of the Direction of Mines in Příbram and installed now in the collection of the Dept. of Mineralogy of the Charles University (Fig. 19).

The sample examined is about 30 × 17 cm in size and comes from the 25th level of the Anna Mine in Příbram, from the Ševčín vein. Basically, it is composed of diabase fragments lined with sphalerite and cemented with siderite.

Macroscopic features that aroused doubt about the normal successive deposition of minerals around rock fragments were the following:

1. Non-uniform thickness of sphalerite fringes around some of the fragments (e.g. in fragments 1, 2, 3 and 4 in Fig. 19).

2. Extension of sphalerite fringes around fragments is not regular in the plane section: e.g. in fragment No. 1 and 2 the ZnS fringe extends in the upward direction, in fragment No. 3 in the downward direction and in fragment No. 4 in an obliquely downward direction.

3. Between some of the fragments (Nos. 5 and 6) is an accumulation of sphalerite.

Observations shown by 1 and 3 above had already proved themselves

valuable as criteria for demonstrating the metasomatic origin of fringes of cockade textures from Polkanová.

Microscopic observations of polished sections, prepared from the specimen examined show that the sphalerite fringe is as a rule separated from the rock fragments by a quartz fringe (Figs. 20, 21).

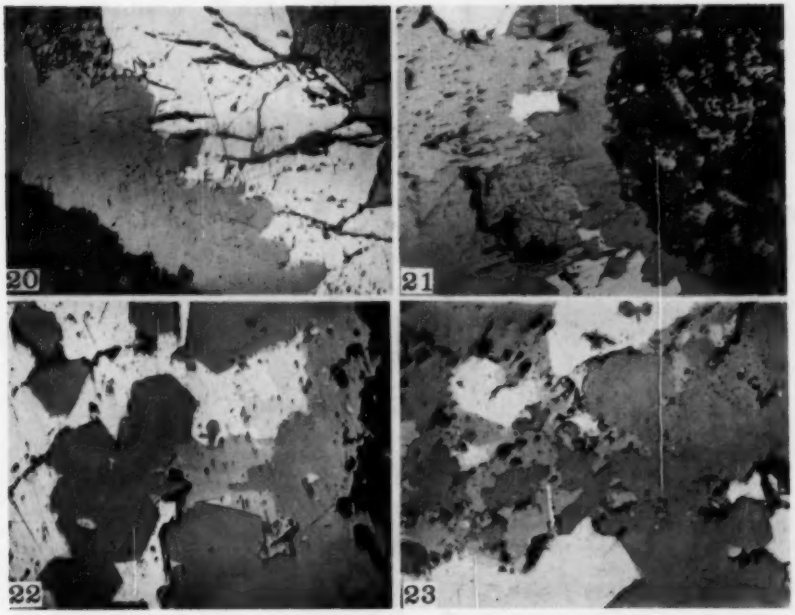
On superficial examination of Figure 20 it might be assumed that the quartz individuals composing this fringe grew as the oldest component in the direction away from the rock fragment and that sphalerite in which these individuals more or less terminate crystallographically, was deposited on quartz in cavities between rock fragments. In the upper left-hand part of Figure 20 it may be seen that at places where the sphalerite mass disappears quartz is equally well bounded against siderite as against sphalerite in the vicinity. After all, even this case would be still explainable from the point

FIG. 19. Cockade texture from the Ševčin vein in Příbram, in which sphalerite fringes around rock fragments were formed by replacement of siderite that cements them. The thin quartz zone between the rock fragments and sphalerite is not visible macroscopically. Natural size about 30 × 17 cm.

of view of normal successive deposition of components around rock fragments: namely it could be assumed that sphalerite did not necessarily crystallize in the cavity in the form of a continuous band on the entire quartz fringe; where sphalerite was not formed, younger siderite was deposited directly on quartz, where sphalerite was present it sat on it as the third, youngest component in the direction away from the rock fragments.

If, however, other places are examined, e.g. in Figure 21, where the sphalerite fringe begins with a small accumulation of ZnS material at the quartz-siderite boundary and increases in the direction into siderite, the view is inevitably reached that the sphalerite fringes could have been formed by selective replacement of siderite from the boundary with quartz. At numerous places good examples confirming this opinion may be found.

One such place is shown in Figure 26, representing an enlarged part of Figure 22 as observed with crossed nicols and making it possible to estimate the relationship of sphalerite to the boundaries of siderite grains. Figure 26 shows clearly that sphalerite is younger than siderite and quartz as it replaces siderite from its boundary with quartz. The replacement along the boundaries of siderite grains is well marked between grains No. 1 and 2, 2 and 3, and 3 and 4. In the last case, it is clearly visible that the solutions arrived along the quartz-siderite boundary and only thence replaced siderite



FIGS. 20 and 21. Microscopic details of a cockade texture (such as in Fig. 19) showing that between the rock fragment (black) and the sphalerite fringe (white) there occurs at some places a relatively rather thick quartz zone (darker gray, with smooth surface). Its more or less idiomorphically bounded individuals protrude into sphalerite or into siderite (lighter gray, with rougher surface) as long as the ZnS zone does not form a continuous fringe all round. The Ševčín vein, Příbram. Magn. 22 ×.

FIG. 22. On the basis of the discussion of Figures 26 and 27, this figure can be interpreted as a complex of perfect quartz metacrysts in siderite, which was to a great extent selectively replaced by sphalerite, giving rise to the "fossil boundary of the 1st stage" in the sense of J. Kutina (12). Black, rock fragment; dark gray, quartz; light gray, siderite; white, sphalerite. The Ševčín vein, Příbram. Magn. 85 ×.

FIG. 23. Replacement of siderite by quartz, at places displaying quite irregular lobe-like boundaries against siderite, and rarely possessing imperfect idiomorphic bounding. Siderite (light gray) is at places replaced by sphalerite (white). Darker gray, quartz. The Ševčín vein, Příbram. Magn. 85 ×.

along the boundaries of its differently oriented grains No. 3 and 4. It may be assumed from the shape and position of a large mass of sphalerite in the area below the relict of grain No. 2 that the replacement proceeded into the area of grains 1, 2 and 3, from a narrow, originally siderite corridor between two juxtaposed large grains or areas of quartz, whence it spread first of all to the sides, beginning with the quatz-siderite boundary and continuing further into the siderite mass along the boundary of grains No. 1 and 2 on one side and along that of grains No. 2 and 3 on the other side. From the point of view of ease of penetration of solutions during selective replacement of siderite the boundary between different minerals (quartz-siderite) appeared favorable, more than grain boundaries of the same mineral (boundaries between differently oriented grains of siderite).

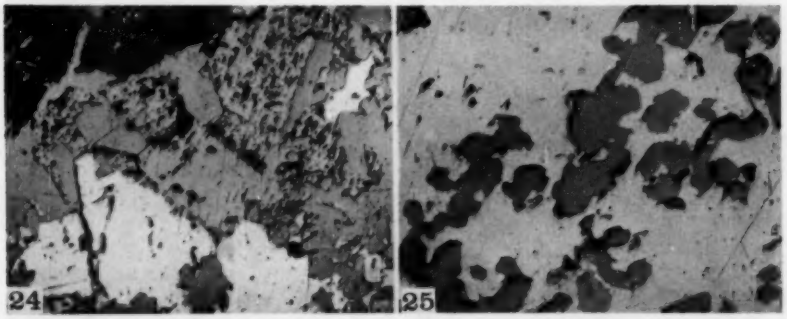


FIG. 24. Replacement of siderite by quartz away from the boundary with a rock fragment, connected with the formation of well defined quartz metacrysts. Siderite is at places replaced by sphalerite. The Ševčín vein, Příbram. Black, the rock fragment; darker gray with smooth surface, quartz; lighter gray with rougher surface, siderite; white, sphalerite. Magn. 23 ×.

FIG. 25. Metasomatic forms of quartz with a tendency to idiomorphic bounding, originally formed in siderite that was totally replaced by sphalerite. The Ševčín vein, Příbram. Magn. 85 ×.

Figure 22, showing a larger part of the polished section than Figure 26, displays a beautifully marked idiomorphic bounding of quartz. In the lower part of Figure 22, the idiomorphic bounding of a large quartz individual against siderite is preserved to a great extent, whereas in the entire left-hand part of this photomicrograph siderite was completely replaced by sphalerite and thus the polished section reveals only quartz grains, idiomorphically bounded against sphalerite.

Similar cases from a mineragraphic investigation of Příbram "Dürrerz" (from the Main Ethelbert Vein) were described by Kutina (12) as "fossil boundaries." In the given cases the original boundary was also represented by quartz and siderite. By selective replacement of siderite by sphalerite or galena, which proceeded from the boundary with quartz, the "fossil boundary of the 1st stage" was formed. Further solutions ascended then along

the boundary of quartz and replaced galena and sphalerite giving rise to boulangerite and to the "fossil boundary of the IInd stage." At places where the replacement by sphalerite and galena did not extend, boulangerite was deposited directly at the expense of siderite. In this case, its boundary with quartz represented only the "fossil boundary of the Ist stage." A comparison with other cases of selective replacement in ores described in

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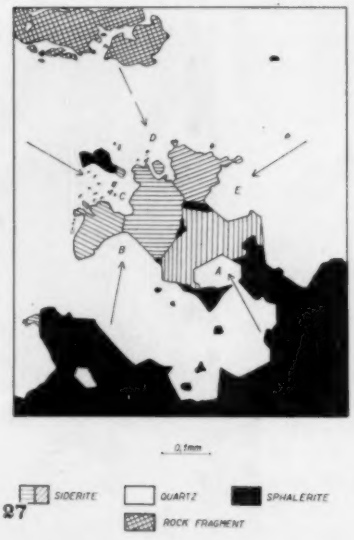

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FIG. 26. Magnified detail of Figure 22 when observed under crossed nicols. Sphalerite selectively replaces siderite away from its boundaries with quartz and further along the boundaries of differently oriented siderite grains. The Ševčín vein, Příbram.

FIG. 27. Replacement of siderite by quartz, which in regions marked B, C, D, E, proceeds with least difficulty in the direction of boundaries of differently oriented grains of siderite, is taken as evidence, together with the optically identical orientation of siderite relicts in the region C, that the idiomorphic bounding of quartz at A, B and E represents the origin of quartz metacrysts. Sphalerite selectively replaces siderite. The Ševčín vein, Příbram.

the literature (1, 2, and others) can be found in the paper of J. Kutina cited above.

The described cockade texture from the Ševčín vein represents a simpler case since here siderite was not replaced by any other ore mineral but sphalerite. The recognition of this process is, however, very important as at places of complete replacement of siderite the origin could be erroneously interpreted as a deposition of sphalerite in cavities between quartz individuals.

Thus we are dealing here with a cockade texture, in which the sphalerite fringes around rock fragments were formed by replacement of siderite oc-

curring originally at the present site of sphalerite. It remains to be solved whether the quartz zone between the rock fragment and sphalerite (or siderite) was also formed by replacement of siderite (similarly as in the cockade textures from Polkanová and Gelnica) or whether this is a special case where quartz and siderite were deposited successively around rock fragments in the first place and only then siderite was replaced by an ore component from its boundary with quartz.

FIG. 28. An example of the shape of simultaneously extinguishing relicts of siderite in quartz from the region C in Fig. 27. The Ševčin vein, Příbram. Magn. 1,540 ×.

FIG. 29. A quartz metacryst penetrating by beak-like extensions into surrounding ankerite. Polkanová, Magn. 140 ×.

Figure 27 supplies criteria for the solution of the above problem. In addition to the replacement of siderite by sphalerite, proceeding both from the boundary with quartz and from the boundaries of differently oriented siderite grains, it may be seen that at four of the five sites (marked A to E) quartz penetrates into the siderite aggregate most deeply at places of contact of its differently oriented grains (in the direction of arrows shown in Fig. 27). At sites A, B and E, quartz is at the same time more or less perfectly bounded with respect to siderite. At E, both an idiomorphic and an irregular bounding of quartz is visible. In the region of D, the quartz displays relicts after replacement of siderite, the largest of which reveals a very marked simultaneous extinction with the neighboring large grain of siderite. In the region of C, are numerous small relicts after siderite replacement, which extinguish simultaneously with the large grain, lying beneath them may be observed in Figure 24. The elongated siderite relict situated above them, displays, too, a simultaneous extinction, the relict being from a part replaced by sphalerite. An example of the shape and distribution of some small siderite relicts from the region C is shown in Figure 28. Another example of replacement of siderite by quartz from the same polished section is shown in Figure 23.

The above-mentioned observations show that the quartz zone around rock fragments was also formed essentially by replacement of siderite and that the more or less idiomorphically bounded quartz grains in Figures 22, 26 and 27 must be considered as metacrysts.

Figure 24 shows places where the replacement by quartz proceeded only in a lesser degree and where, therefore, a sufficient amount of siderite is still preserved in the immediate vicinity of the rock fragment. Here, too, idiomorphic bounding of quartz against siderite took place.

The last figure (Fig. 25) represents an example of a perfect selective metasomatism of siderite: The set of quartz grains represents, by their shape and partial parallel arrangement, metasomatic forms formed originally by replacement of siderite which was then totally replaced by sphalerite. It is worth while to compare some of these quartz forms with rather similarly bounded forms of quartz in unreplaced siderite in Figure 23.

The cockade texture from the Ševčín vein was formed by a similar process as the cockade textures from Polkanová and Gelnica. The rock fragments were originally cemented only by siderite which was then successively replaced by quartz and sphalerite, giving rise to layers. During the formation of the quartz fringe a partial replacement of the outer part of the rock fragments may have taken place.

CONCLUSIONS

Three cases of cockade textures are described, which were not formed by simple successive deposition of minerals around rock fragments as had been assumed heretofore.

In the cockade texture from Polkanová the layers are formed by quartz and tetrahedrite, in the cockade texture from the Ševčín vein in Příbram by quartz and sphalerite, and in the sample from Gelnica by quartz only. Quartz

fringes are older than the ore components and were formed from solutions ascending along the boundaries of rock fragments with the cementing siderite during which process the adjacent part of siderite and the outer parts of the rock fragments were replaced. The outer boundary of rock fragments thus became a difficult channelway for further ascent of solutions. Their new ascent then took place along the boundary of quartz and siderite whence siderite was replaced giving rise to another layer, formed by tetrahedrite (in Polkanová) or sphalerite (in Příbram).

It is the authors' opinion that the rock fragments, due to replacement of their outer parts, could have easily lost contact with one another and their relicts become independent (the more so with deeper replacement of their outer part by quartz). During this process it is not necessary to assume gravitational movement of rock fragments since they were firmly supported by the cementing component—siderite, which was not replaced at the same time and in the same degree at all points of contact with the rock fragments.

This process of origin of cockade textures was recognized on the basis of macro- and microscopic observations, the following features appearing as fundamental for characterization.

Principal macroscopic features:

1. Irregular thickness of the layer of ore mineral around an individual rock fragment (Polkanová, Příbram).
2. Significantly different thickness of the layer of the ore component in different rock fragments (Polkanová, partially Příbram).
3. Widening of the ore fringes around rock fragments is not regular in the plane section (in some fragments the ore fringe widens in the upward, in others in the downward direction etc.) (Příbram).
4. Accumulation of the ore material between some close-lying fragments (Polkanová, Příbram). The same is apparent in the case of quartz fringes of some fragments from Gelnica.
5. Projecting of the layers or their continuation in the form of veinlets in the direction into the main cementing component (tetrahedrite in the samples from Polkanová, quartz in the sample from Gelnica).

Principal microscopic features:

The main cementing component, siderite, was in all cases investigated (Polkanová, Gelnica, Příbram) replaced by minerals forming fringes around rock fragments. The following fundamental criteria were employed in recognizing this process:

1. Replacement along the grain boundaries (by tetrahedrite and quartz in Polkanová, by quartz in Gelnica, by sphalerite in Příbram). Very common.
2. Replacement along the cleavage planes [11] (by tetrahedrite and quartz in Polkanová). Common.

[11] With a very marked change in the course of veinlets amounting to the angle subtended by the cleavage directions (not shown in figures).

3. Replacement across the grains without apparent relationship to the grain boundaries and to the cleavage (by tetrahedrite in Polkanová). Less common.

4. Simultaneous extinction of small relicts after replacement enclosed in the replacing mineral (siderite relicts in quartz from Polkanová and Příbram).

5. Continuation of the layer into the main cementing component in the form of metasomatic veinlets, the connection of which with the lining band was observed in the polished section (tetrahedrite in Polkanová, quartz in Gelnica).

6. Formation of metacrysts of quartz in siderite. Criteria for their recognition are shown below. (Gelnica, rather rare in Polkanová, very common in Příbram).

Material from each locality is distinguished by certain specific features:

E.g., quartz in polished sections from Polkanová projects into siderite by long metasomatic veinlets, particularly along grain boundaries and cleavage planes, whereas the formation of quartz metacrysts is considerably limited here. On the other hand, in polished sections from Příbram cockade textures, perfectly bounded quartz metacrysts are very common, and the projection of quartz into the siderite mass in the form of veinlets is practically absent. In spite of this, however, even here metasomatism appears to take place more readily in the direction of boundaries of differently oriented siderite grains.

In the polished section from Gelnica, quartz projects into surrounding siderite in a few places in the form of veinlets, and the replacement of siderite by quartz along the grain boundaries is well marked. The formation of quartz metacrysts is restricted here mostly to the less perfect idiomorphic bounding of terminal parts of quartz individuals in the direction into siderite.

It follows from the above that the replacement of siderite by quartz can be morphologically different at different localities but that it bears some common features and can be well recognized with the aid of genetic criteria.

As far as ore minerals are concerned, no generalization can be drawn since no identical ore components were available for comparison. It is interesting nevertheless that tetrahedrite in polished sections from Polkanová projects much farther from its layers into the siderite aggregate, than does sphalerite in polished sections from Příbram. In the last-named case, replacement proceeds preferentially along the contact of quartz with siderite and then along the boundaries of siderite grains, but in general its progress is more uniform than that of the replacement of siderite by tetrahedrite in Polkanová.

On the basis of the above results the authors are of the opinion that it would be desirable to revise the existing descriptions of cockade textures in the literature. It cannot be excluded that some of them could have originated in an analogous manner as the texture from Polkanová, Gelnica and Příbram described here.

The paper also represents a contribution to the study of veinlets that have a segmented character in the plane section ("segmented veinlets," cf. Bastin

(2). It was shown that minerals forming the segments in the segmented veinlets of metasomatic origin can be of different age.

In the genetic discussion of the idiomorphic bounding of quartz in siderite the following criteria were considered fundamental for the recognition of quartz metacrysts:

1. Preferential development of idiomorphically bounded quartz grains in the direction of boundaries of differently oriented grains of siderite (some places in the polished sections from Příbram, cf. Fig. 27).

2. Continuity of idiomorphically bounded quartz grains with a quartz mass which, in the immediate vicinity, replaces siderite along the boundaries of its differently oriented grains (Příbram, Fig. 27). Such continuity was very abundant in the polished section from Gelnica, as well (cf. Fig. 18 with Fig. 17).

3. Projecting of idiomorphically bounded quartz grains into surrounding siderite (e.g. small projections of the quartz individual in Fig. 18 from Gelnica and the right-hand side of Fig. 26 from Příbram). In a few cases, the quartz individual continues in the form of a narrow veinlet along the boundaries of siderite grains (Gelnica, Fig. 18).

4. Continuity of the more or less idiomorphically bounded quartz crystals with the quartz mass containing simultaneously extinguishing siderite relicts, showing replacement of siderite by quartz (Příbram, Fig. 27). Relicts after replacement of siderite are rarely present in the very metacrysts of quartz (e.g. Fig. 12 from Polkanová).

5. Immediate continuity of idiomorphically bounded quartz grains with the quartz mass replacing siderite from its contact with rock fragments (Příbram, Fig. 27; Gelnica; a spatial relationship exists undoubtedly in Polkanová, as well).

6. Development of an incomplete crystal of quartz from a quartz-tetrahedrite veinlet replacing siderite (Polkanová, Fig. 12) or in the course of the veinlet (Polkanová, Fig. 10).

A. D. Genkin in his paper "On metacrysts" (5, p. 193–221), which represents the hitherto most comprehensive analysis of metacrysts in ores, presents a number of characteristic features for their recognition. Of these, the following are either identical or related to our observations: inclusions of surrounding minerals in the metacrysts (particularly inclusions with identical optical orientation); connection of some metacrysts with the boundaries of grains of the older component; continuity of idiomorphic bounding with a veinlet of the same mineral; small outgrowths at crystal corners [12] appearing in some well developed metacrysts. It is significant for the recognition of metacrysts (according to A. D. Genkin) that in ores, even in a single polished section, simultaneous occurrence both of damaged, particularly imperfectly developed forms, and of beautifully developed metacrysts of the same mineral even without any inclusions, is very abundant. This last-named conclusion

[12] For the sake of comparison with this observation of A. D. Genkin a photomicrograph of a quartz metacryst in ankerite from Polkanová displaying remarkable beak-like projections is shown in Fig. 29. The detail itself does not originate from the specimens containing cockade textures but it also belongs to the Hrča vein I.

is in full agreement with our observation, particularly from polished sections of the cockade texture from Příbram (cf. Fig. 22 and 23). As far as quartz metacrysts are concerned, A. D. Genkin describes only cases when SiO_2 was bounded idiomorphically in sulfidic ore minerals and not in siderite, unlike in the examples described.

The formation of imperfect quartz metacrysts in siderite was already recognized earlier by Kutina (12) in polished sections of "Dürrerz" samples from the Main Ethelbert Vein in Příbram.

ACKNOWLEDGMENT

In conclusion the authors wish to express their thanks to Professor J. Koutek for the stimulus to study cockade textures from Polkanová and for providing valuable material from that locality, as well as for valuable comments and interest in the work undertaken. We are indebted to Dr. M. Štemprok for reading critically the manuscript, for comments and for drawing our attention to some literature sources. We are grateful to Dr. Z. Pouba for making it possible for us to examine cockade texture samples in the collections of the Dept. of Mineral Deposits of the Charles University and for providing us with several samples for detailed investigation.

The photograph in Figure 1 was made by V. Šilhan, that in Figure 19 by M. Hatláková. The remaining figures (both photomicrographs and drawings) were prepared by the authors.

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THORIUM MINERALIZATION IN THE LEMHI PASS AREA, LEMHI COUNTY, IDAHO

ALFRED L. ANDERSON [1]

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ABSTRACT

The thorium mineralization in the Lemhi Pass area of southeastern Lemhi County, Idaho, is directed along simple to complex shear and fracture zones, and reopened copper and gold-quartz veins and lodes, in impure quartzitic and phyllitic rocks of the Precambrian Belt series. Some of the shear and fracture zones are more than 40 feet across and comprise broad zones of irregularly mineralized rock reaching distances to 2,000 feet in length. These zones contain notable concentrations of thorium and rare-earth elements along with considerable amounts of barium, alkali metals, calcium, iron, phosphorus, sulfur, and silicon and meager amounts of columbium, uranium, and perhaps other related elements. Minerals identified so far include thorite, allanite, monazite, xenotime(?), euxenite(?), apatite, specularite, barite, alkali feldspar, calcite, biotite, phlogopite, sericite, chalcedony, and quartz. The most characteristic minerals are the thorite, specularite, barite, and quartz. The specularite and thorium-bearing minerals are intimately associated and were introduced into the deposits after the micas and in advance of the barite, feldspar, calcite, and quartz. Except for the specularite and quartz and in part the barite, feldspar, calcite, and thorite, the minerals are not distinguishable without the microscope.

Some of the deposits contain several percent thoria and comparable amounts of rare-earth oxides, but the average is generally under 1 percent.

[1] Published with permission of the Director, Idaho Bureau of Mines and Geology. Presented before the Society of Economic Geologists, San Francisco, February 1959.

The area has an appreciable reserve of lode thorium. Some of the deposits are in or are being brought into production.

INTRODUCTION

FAMED as the site where Sacajawea, the young Indian woman, guided the Lewis and Clark Expedition across the Continental Divide in 1805, Lemhi Pass has become more than historically significant through recent discovery of important thorite-bearing lode deposits. Subsequent exploration has uncovered a number of promising deposits and has indicated that the area has an appreciable reserve of thorium of important economic worth.

Since these deposits have received little more than cursory geologic study, such data as are available are incomplete and, except for the preliminary study by the writer (1, p. 45–74), include very little on the mineralogic and genetic aspects of the mineralization. Aside from the commercial attributes, these deposits have much to offer of scientific interest.

GEOGRAPHIC SETTING

Astride the Continental Divide, the Lemhi Pass area is partly in Idaho and partly in Montana, the Divide marking the boundary between the two States (Fig. 1). The Idaho part is in southeastern Lemhi County about 26 miles airline southeast of Salmon. The remainder, which is not included in the present investigation, is in Beaverhead County, Montana.

The area studied covers the western slope of the Beaverhead Mountains from the Lemhi River to the crest and Continental Divide (Fig. 1). Although elsewhere high and rugged, the mountains locally are relatively subdued and are characterized by rounded ridges that rise steeply from narrow valley floors. These ridges reach an altitude of about 8,000 feet at the Pass, nearly 2,000 feet below the bordering ridges but more than 3,000 feet above the floor of Lemhi Valley. The relief is much less on the Montana side. The area is drained by Agency Creek and its tributaries and by lower Pattee Creek, both of which join the Lemhi River. The drainage on the Montana side is principally by Trail Creek and North and South Frying Pan Creeks (Fig. 1), eventual tributaries of the Missouri River.

The area is within easy reach of Salmon over State Highway 28. At Tendoy a graded road extends up Agency Creek across Lemhi Pass into Montana. An unimproved road branches from the Agency Creek road about a mile from Tendoy and gives access to Pattee Creek.

GEOLOGIC SETTING

The deposits in the Lemhi Pass area are contained in broadly folded and complexly faulted, impure quartzitic and phyllitic rocks belonging to the Precambrian Belt series. These rocks are intruded by scattered small dioritic and lamprophyric bodies of uncertain but probable late Cretaceous or early Tertiary age. On the lower slopes and in the Pass these ancient sedimentary rocks are partly blanketed by Tertiary volcanics. Near the Lemhi River, the volcanics and older rocks pass beneath Tertiary lake beds. All

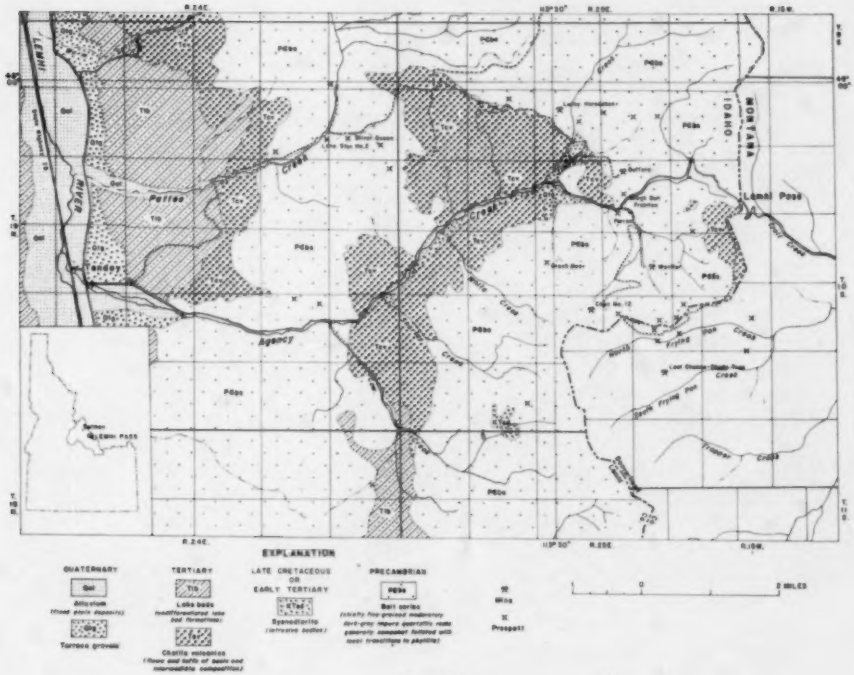

FIG. 1.

rocks are covered locally by terrace gravels and alluvium of Quaternary age (Fig. 1).

HISTORICAL SKETCH

The Lemhi Pass area has long been known for its copper and gold mineralization, but it was not until the radiometric surveys for uranium made by Vhay (7) in 1949 and by Trites and Tooker (6) in 1950 in behalf of the U. S. Atomic Energy Commission that some of the copper and gold veins were found to contain thorium. This discovery prompted active participation of the Federal Government in the exploration of two of the showings that then seemed to offer the most promise. Funds provided by the Defense Minerals Exploration Administration from 1952 to 1955 were used to explore the showings on the Wonder lode claim by means of bull-dozed trenches, drifts and crosscuts on two levels, and by three diamond-drill holes. Some diamond drilling (two holes) was also done on the Last Chance-Shady Tree lode across the Divide in Montana (Fig. 1).

The discovery of thorium and the early exploration attracted widespread attention and led to a wave of prospecting with the Geiger and scintillation counters and to the resultant location of many hundreds of claims, some of which proved to possess deposits of major consequence. Subsequent ex-

ploration involved extensive use of the bull dozer. There then followed consolidation of holdings through purchase and stock transfer so that now the control of most of the deposits is in the hands of a few companies and individuals. Some thorite was mined and concentrated in 1959; but operations were then still largely in the planning stage, with more extensive operations to come in 1960.

CHARACTER OF THE DEPOSITS

Although these deposits are to be regarded primarily as thorite deposits, they also contain an appreciable concentration of rare-earth elements, particularly those of the cerium and yttrium groups, and very minor to negligible amounts of uranium and columbium. At present the only interest is in the thorium.

The deposits show some variation in structural and mineralogical behavior, depending on whether the thorium was introduced into earlier-formed and otherwise unrelated veins and lodes or into later, independent zones of shearing and fracturing. Earlier workers apparently failed to appreciate that the thorium mineralization is younger than, and independent of, the gold and copper mineralization and made little, if any, distinction between the two groups of deposits. According to the principal mineral constituents, Sharp and Cavender (5, p. 1555) separated the deposits into four types of quartz veins: including (1) veins containing copper-bearing sulfides, (2) veins containing hematite, (3) veins containing barite, hematite, and thorite, and (4) veins containing copper-bearing sulfides and thorite. Such a classification takes care of all veins in the area irrespective of time of origin, and has generally been accepted by later workers (8, 1958, p. 36), who stress the occurrence of quartz-barite-hematite, quartz-hematite, and quartz veins and the presence of sparse to abundant sulfides in some of the quartz veins. Note has also been made of the presence of thorite in fractures of a shear zone at the Wonder lode, in which virtually no other vein minerals are represented.

Most of the deposits discovered during the late wave of prospecting are not associated with the earlier quartz and copper-bearing veins but are along independent zones of shearing and fracturing. These may be more appropriately characterized as mineralized shear and fracture zones with ore introduced partly by filling but largely by replacement. These comprise the lodes of greatest promise.

Because of their mineral associations and structural relations, these deposits may be classed as hydrothermal veins and lodes composed of a unique group of minerals, which are in part more characteristic of igneous rocks and pegmatites than of veins.

STRUCTURAL RELATIONS

The thorite deposits are distributed along a broad belt about 6 miles wide that crosses the area in a southeasterly direction (Fig. 1). This belt emerges from beneath a cover of volcanic rocks and lake beds just north of Pattee Creek and continues its southeasterly course across the Continental Divide and

on for some distance into Montana, concealed here and there by patches of volcanic rocks (Fig. 1).

Within this broad belt of mineralization the deposits are contained along shear and fracture zones whose trend for the most part accords with that of the broad belt. Except for a few deposits along or close to the Continental Divide, the individual shear and fracture zones trend about N 60° W, in some places close to N 70° W, and less commonly N 30° W. These zones generally dip steeply southwest, but a few dip northeast. Some of the deposits near the Continental Divide that do not conform with the general northwesterly trend bear in east-northeasterly directions.

With few exceptions, the shear and fracture zones are relatively broad, measuring up to 40 to 60 feet, exceptionally 120 feet across. The mineralization, however, rarely extends through the full width of the zone, nor along the full length. The length of these zones is measurable in hundreds and in some cases several thousands of feet; but, with some notable exceptions, the mineralization along them is sporadic and the individual deposits are comparatively short with lengths from a few hundred to less than 1,000 feet.

The older quartz and copper-bearing veins and lodes are controlled by earlier shearing and fissuring; but where these deposits were reopened by the structural movements that initiated the thorite mineralization, they contain some thorite and associated minerals. Because these earlier, structurally resistant quartz and quartz-sulfide veins did not respond so readily to fracturing as did the weaker bedded rocks, they are generally not so richly nor so extensively mineralized with thorite as are the later independent shear and fracture zones.

MINERALOGY

Summary Statement

The minerals considered are only those associated with the thorite mineralization and do not include any that may have been inherited from invaded gold- and copper-bearing quartz veins and lodes. The thorium mineralization is characterized by a distinctive group of minerals, which includes not only thorite but also lesser amounts of several other thorium-bearing minerals, as well as a number of more ordinary minerals. Although the thorite is regarded as the diagnostic mineral of the deposits, its place is taken in one deposit by allanite and in several others, at least in part, by euxenite(?). The thorite is invariably accompanied by specular hematite and quartz and generally by barite, feldspar, apatite, and by sparse monazite and xenotime(?). The complete list of minerals is tabulated below.

Silicates	Sulfates	Oxides
Thorite	Barite	Euxenite(?)
Allanite		Specularite
Biotite	Carbonates	Magnetite
Phlogopite	Calcite	Quartz
Sericite		Chalcedony
Epidote	Phosphates	
Albite	Apatite	Sulfides
Microcline	Monazite	Pyrite
	Xenotime(?)	

Few of these minerals are recognizable without the petrographic microscope. Those that are include specular hematite, feldspar, calcite, and quartz; but the thorite, barite, allanite, and pyrite, except rarely, and the others are not distinguishable by the unaided eye. The microscope is essential for mineral identification and must be used for each deposit in which the complete list of minerals is wanted.

As most of the deposits are exposed in surface cuts, the minerals listed above are generally found with abundant hydrous iron oxides, mostly yellowish-brown goethite, less commonly blackish manganese oxides. In some deposits the secondary iron oxides occur as dense, compact seams and masses; in others, as minute disseminations, giving the vein material a brownish, jasperoid appearance. With the oxidation products are variable amounts of hydrated thorite or hydrothorite.

Descriptive Features

Biotite is one of the minor minerals and is not always evident to the unaided eye. Some of it may represent an inheritance from the country rock, but much of it is so intimately associated with the lode minerals that it must have been introduced with them, probably at the beginning of the mineralization. It is revealed rather sparingly under the microscope, most abundantly with the thorite and specular hematite.

The biotite grains are small, show moderate absorption, and in part may be somewhat bleached. They are irregular in outline and are commonly cut off or penetrated by crystals of specular hematite and by any accompanying thorite and monazite. At the Lucky Horseshoe the biotite is penetrated and replaced by allanite. It is generally sparse or wanting in aggregates of barite, feldspar, and quartz, or occurs in them only as small remnant inclusions.

Phlogopite is also closely associated with the thorite mineralization, but is less abundant than biotite and may be more characteristic of the deposits containing calcite than in those in which calcite is lacking.

Except for its very weak absorption and only faintly discernible pleochrism, it is much like the biotite in its properties with some tendency, however, to develop radially. Like the biotite, it is penetrated and replaced by specularite and other minerals.

Sericite occurs in some of the deposits. It is a sparse mineral and is nowhere noticeable, except in the lode at the Cago No. 12, where some of the coarser grains in the more marginal parts of the deposit may be observed by the unaided eye. This colorless mica occurs mainly as minor, very thin, non-persistent seams in those parts of the quartzose lodes invaded by the thorite and associated minerals. Like the biotite and phlogopite, it is an early mineral and is penetrated and replaced by thorite and specularite.

Thorite is the economically important mineral in the district, although it is not the only source of thorium. It has a widespread distribution and has been found as an essential constituent of all but two or three of the deposits that have been examined microscopically. Any deposit that shows radioactivity is presumed to contain thorite, but its crystals or grains are

rarely distinguishable without the microscope. In some deposits small, reddish grains or colorations may suggest thorite; but only in some very rich ore at the Cago No. 12 may the grains be detected by the eye alone, although partly masked by specularite and coatings of brownish, hydrated iron oxides.

The composition of thorite is usually expressed as $ThSiO_4$, but the mineral may contain appreciable amounts of isomorphous rare earths of the cerium group, commonly some yttrium, uranium, and other elements with atomic radii similar in size to that of thorium. The thorite in the Lemhi Pass area seems to contain most of these other elements. Analysis of a sample of thorite-rich ore at the Cago No. 12 made by the U. S. Bureau of Mines (1, p. 56) revealed 13.5 percent combined thoria and rare-earth oxides, which on breakdown were found to be composed of 43.8 percent thoria (ThO_2), 2 percent yttrium oxide, and 44.2 percent combined oxides of the cerium group. Microscopic examination of some of the rich ore disclosed a little more thorite than specularite, minor monazite, and scant xenotime (?). The monazite content is far too small to account for all the rare earths revealed by the analyses. Another analysis of selected samples of the thorite-rich hematite is reported by Moen (3, p. 20) to contain 6.85 percent ThO_2, 0.147 percent U_3O_8, and 44.4 percent iron. Although the associated monazite would account for a part of the rare earths and perhaps for some of the thorium, it could not account for all and hence the thorite must be credited with a considerable content of rare-earth elements and a small amount of uranium.

Under the microscope the thorite appears as short, square prisms with reddish-orange border zones, the coloration generally extending through all but the center of the otherwise colorless crystals. The thorite is thus partly to completely metamict and is largely recognized by its reddish-orange decomposition products. It generally occurs as scattered crystals (Figs. 2, 11), but here and there the crystals occur in clusters (Fig. 3).

The thorite shows a marked preference for the micaceous parts of the deposits and for specular hematite and monazite. Its grains are commonly sheltered by or enclosed within aggregates of specularite, the specularite surrounding and locally penetrating the thorite (Fig. 3). It may also be caught in and partly mantled by and in places penetrated by euhedral crystals of monazite. The thorite along with the monazite and specularite extend into and replace the micas and the sheared and fractured rock. Each in turn is stranded or held as remnant inclusions within grains and aggregates of barite, feldspar, calcite, and quartz (Fig. 2).

Allanite, another source of thorium and rare earths, has a very restricted distribution and is abundant only at the Lucky Horseshoe. It is a sparse accessory in some of the immediately adjacent deposits. Except for a little monazite, the allanite is the only radioactive mineral at the Lucky Horseshoe, the thorite being completely excluded.

A cerium-bearing epidote, allanite may contain considerable amounts of the cerium-group elements and thorium and its formula may be expressed as $(Ca,Ce,Th)_2(Al,Fe,Mg)_3Si_3O_{12}(OH)$. At the Lucky Horseshoe the allanite

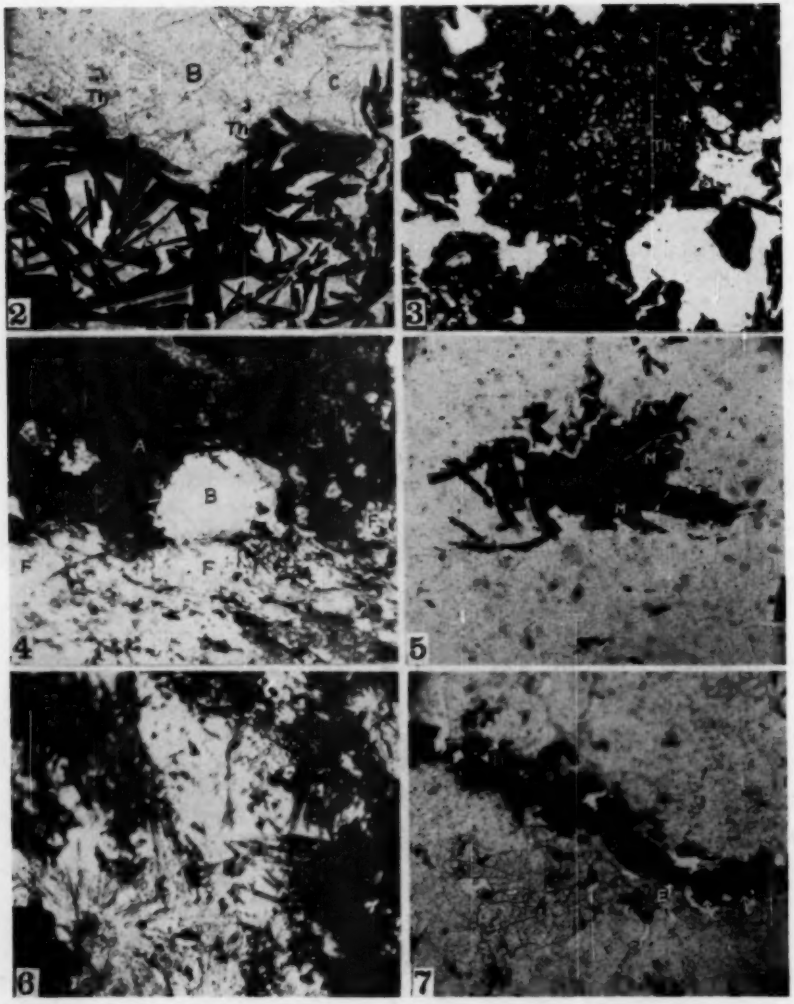

FIG. 2. Black, bladed crystals of specularite and scattered crystals of thorite (Th) invaded but largely unreplaced by light-colored barite (B). Barite and locally specularite are penetrated by calcite (C). Thorite crystals enclosed by specularite are scarcely distinguishable. Uncrossed nicols. × 47.

FIG. 3. A cluster of thorite grains (Th) surrounded by black specularite. White areas are holes in section. Clusters of thorite grains are not so common as the scattered grains. Uncrossed nicols. × 70.

FIG. 4. Large, dark-colored allanite crystal (A), irregularly penetrated and replaced by barite (B) and by aggregate feldspar (F). The feldspar also invades

is strongly radioactive and is presumably relatively rich in thorium and rare-earth elements. Analytical returns on material submitted by the owner to commercial analysts tend to confirm the high thoria and rare-earth content. Being so relatively abundant at the Lucky Horseshoe, the allanite may be recognized without the microscope, mainly by the dark-gray "hornblendic" appearance it imparts to zones of mineralized rock. Under the microscope it is readily identified by its brown color and by its marked brownish and brownish-red pleochroism. Some of the allanite has partly inverted to a reddish amorphous metamict.

The allanite occurs sporadically throughout much of the broad zone of sheared phyllite at the Lucky Horseshoe. Its well-shaped crystals penetrate and replace the quartz and micaceous minerals of the phyllite and are in turn penetrated by crystals and aggregate seams of specularite and, in places, by monazite. It also shows engulfment and replacement by barite, albite, microcline, and quartz (Fig. 4). The allanite plays the same role in this deposit as does the thorite in the other deposits.

Epidote is another mineral of limited distribution and may be restricted largely to the Lucky Horseshoe where it occurs as sparse, microscopic grains, apparently more or less closely associated with the allanite.

Monazite, another probable source of thorium, is quite subordinate to the thorite. It is sparsely represented in all the deposits examined microscopically. Its exact composition has not been determined; but from the kinds and quantities of rare earths known to be present in the deposits, its composition may not be far from the customary formula $(Ce,La,Nd,Pr,Th)PO_4$.

The grains of monazite are small, only a little larger than those of the thorite, and cannot be discerned by the unaided eye. It generally occurs as small but well-shaped crystals, unless it has been engulfed within grains or aggregates of barite, feldspar, and quartz, in which case its outlines may be irregular and its appearance that of remnants of once much larger and more perfectly formed grains (Fig. 5). Its partial mantling of the thorite and its penetration by specularite, barite, and other minerals fixes its position as early in the succession and indicates that it is one of the earlier-formed minerals, perhaps only a little younger than the thorite.

Apatite, another mineral characteristic of the thorite mineralization, has

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the barite and retains within itself small, included crystals and remnants of specular hematite (lower part of the section). Uncrossed nicols. × 25.

FIG. 5. Remnant specularite (black) and closely associated monazite crystals (M) engulfed in aggregate feldspar (light). Some of the monazite occurs as inclusions within the hematite, suggesting that it is somewhat older than the hematite. Uncrossed nicols. × 47.

FIG. 6. Phantom rosettes of apatite and remnants of other minerals included in late quartz (light) that penetrates and forms an essential part of the thorite deposits. Uncrossed nicols. × 47.

FIG. 7. Remnant specularite seam (black) loaded with euxenite (?) grains (E), distinguished by somewhat lighter color, and remnant grains of apatite (A) in feldspar. The euxenite protected by the specularite generally escaped replacement by the aggregate feldspar. Uncrossed nicols. × 47.

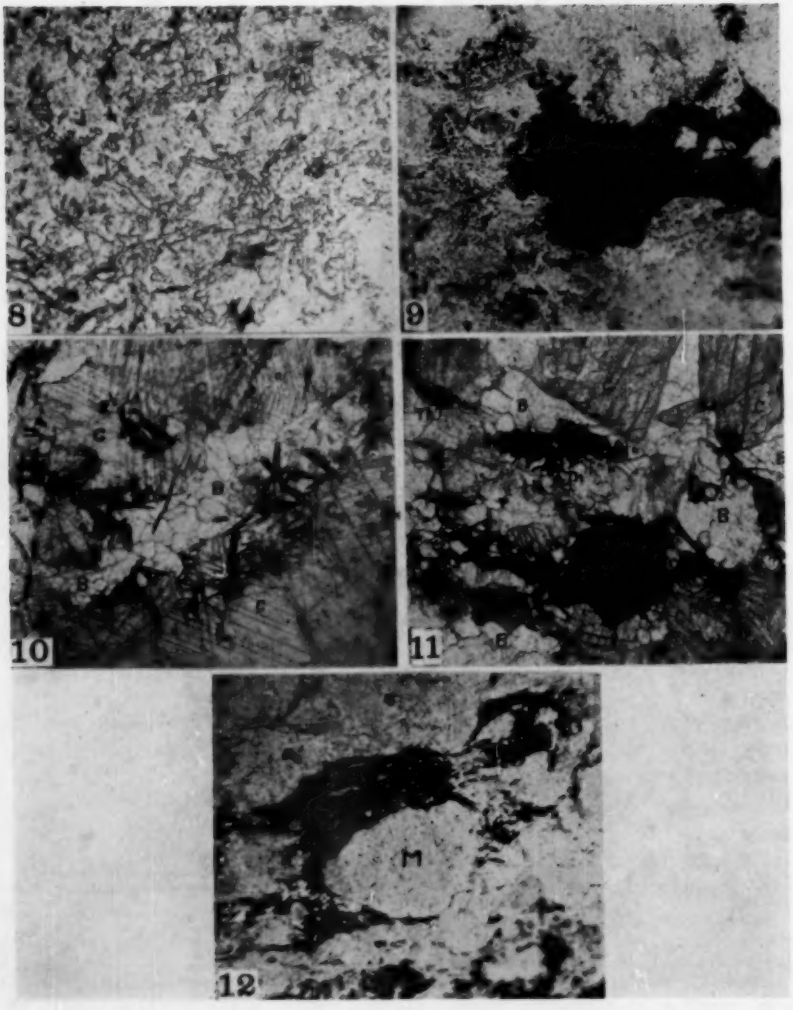

FIG. 8. Feldspar aggregate (light) littered with the unreplaced remains of apatite crystals (slightly darker and higher relief). Uncrossed nicols. × 25.

FIG. 9. Country rock (light) littered with tiny specularite grains entered and replaced by large grains of specularite associated with the thorite mineralization. Uncrossed nicols. × 47.

FIG. 10. Group of black specularite crystals invaded and in part retained as inclusions within an aggregate of nearly white barite grains (B) with both then held as inclusions in invading, more darkly appearing calcite (C). Specu-

a sporadic distribution, abundant in some deposits, sparse or even lacking in others. It occurs as microscopic crystals, which in some deposits are long, almost needle-like (Fig. 6) and in others, short and tabular (Fig. 7). Except for their distinct cross-partings, some of the short, tabular grains tend to resemble the barite grains. The apatite may form isolated crystals, but generally the crystals are clustered or so grouped as to form granular aggregates.

The apatite occurs in close association with the monazite and thorite and like them is commonly penetrated by specularite and held as remnant inclusions in barite, feldspar (Fig. 8), and quartz (Fig. 6).

Xenotime(?) occurs as sparse, microscopic grains in most of the deposits, in all cases closely associated with the thorite and monazite. Xenotime is essentially yttrium phosphate (YPO_4), but many rare-earth elements as well as uranium and thorium may substitute for a part of the yttrium. Until the mineral has been isolated for X-ray and spectrographic study, its precise composition and identity must be held in abeyance. It is reported to be present with thorite and uranium in a mineralized shear zone near the Last Chance-Shady Tree lode in Montana (3, p. 23). The presence of this mineral in the Lemhi Pass deposits could account for at least some of the yttrium reported in the thorite ores.

The suspected xenotime occurs as sparse, strongly birefringent, zircon-like grains that show parallel extinction and thus are not to be confused with the monazite crystals with their somewhat different shape and inclined extinction.

Its constant close association with monazite and thorite suggests that its age is about the same as theirs, perhaps more or less contemporaneous with the monazite. In further confirmation of this is the fact that it, like the thorite and monazite, may be stranded as inclusions in barite, feldspar, and quartz.

Euxenite (?) has been noted in a number of thin sections and seems to be widely but sparsely distributed through many of the deposits, with somewhat greater concentration in deposits near Agency Creek and particularly in the Black Bear deposits on the high slope south of Agency Creek (Fig. 1). It is exceptionally abundant in the Black Bear deposits and may be responsible for most of the radioactivity there and the source of most, if not all, the thorium.

Euxenite is a radioactive mineral containing essential columbium, yttrium, cerium, uranium, thorium, and other metals. Its composition is commonly expressed by the formula $(Y,Ca,Ce,U,Th)\ (Cb,Ta,Ti)_2O_6$. A semiquanti-

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larite tends to resist replacement by both barite and calcite, but barite offers little resistance against the calcite. Uncrossed nicols. × 25.

FIG. 11. Specularite (black) and thorite (Th), in part within the specularite, occurring as included grains and crystals in barite (B), with barite and included minerals invaded by the more darkly colored calcite (C) which in part develops its own rhombohedral form against the barite. Uncrossed nicols. × 47.

FIG. 12. Group of black specularite crystals penetrated and replaced by a porphyroblastic-like aggregate of microcline (M), a relationship which indicates that the specularite is older than the feldspar. Uncrossed nicols. × 25.

tative, spectrographic analysis of ore from the Black Bear made through the courtesy of the U. S. Bureau of Mines, Albany, Oregon, indicated 0.2 percent yttria, 8.0 percent columbic oxide, and 0.1 percent tantalic oxide. Microscopic examination of the ore before it was sent for spectrographic analysis showed grains of the mineral enclosed in a seam-like body of specularite (Fig. 7). Positive identification of the mineral as euxenite is withheld until confirmation may be made by X-ray studies.

Because of its black color and intimate association with specularite, the euxenite(?) can not be distinguished without the microscope. In thin section it appears as short, rather broad prismatic crystals with parallel extinction. These crystals occur in parallel or slightly radial aggregates, which appear yellowish-brown in transmitted light. The mineral is partly metamict and shows some breakdown into blackish decomposition products.

Although isolated aggregates of the euxenite(?) have been observed, most of the grains are completely enclosed within veinlets and masses of specularite (Fig. 7). Its affinity for the specularite seems to be even greater than that of the thorite. No thorite was observed with the euxenite(?) at the Black Bear, but sparse grains of monazite and xenotime were present in areas outside the specularite masses. Elsewhere the euxenite is quite subordinate to the thorite. The relations of the euxenite(?) to the barite, feldspar, and quartz are the same as those of the thorite, monazite, and specularite.

Specularite, as characteristic of the mineralization as the thorite, occurs in variable amounts in all deposits, showing a sporadic distribution and no conspicuous abundance, except in scattered pockets. Its presence in the deposits is generally looked upon with favor as an indicator of high radioactivity.

The specularite is characterized by its platy or micaceous form (Fig. 2). It tends to occur as crystalline aggregates in discontinuous seams or veinlets and in small, irregular masses (Fig. 5). Its grain size varies considerably from place to place, from microscopic to grains up to one fourth of an inch long. Most of the grains are distinctly visible without the microscope, but those that are not suggest their presence by the dark color imparted to the ore.

Because of the way it occurs with and surrounds the thorite and encloses and merges with the euxenite(?), the specularite must have been deposited almost contemporaneously with them. This specularite is not to be confused with very minute grains contained in and inherited from some of the country rock (Fig. 9). Like the radioactive minerals, the specularite has in places been engulfed in barite, feldspar, calcite, and quartz, retained without change or left as meager to abundant remnant inclusions (Figs. 3, 4, 10).

Magnetite is not a characteristic mineral of the deposits and is generally absent. Where present, it is in deposits that contain calcite and then only sparingly. It does not appear to be directly associated with the thorite and related radioactive minerals, but seems linked to the calcite and to have been added during later stages of the mineralization.

Barite is another pertinently diagnostic mineral; and, although not recognized in all deposits, it is nevertheless an essential part of the thorium min-

eralization. It is widespread in distribution and relatively abundant. Its abundance in some deposits has prompted the designation of the quartz-barite-hematite group of veins (8, p. 36). The microscope confirms its presence in nearly all deposits.

In some deposits the barite is coarsely crystalline and is readily recognized by the unaided eye but generally its grains are small and can be detected only with the microscope. Its presence may be inferred in many deposits from the weight of the ore material.

Under the microscope the barite is revealed as broad, granular aggregates (Fig. 10), less commonly as scattered grains. These grain and grain aggregates penetrate irregularly into the thorite-specularite areas and may hold these and other closely associated minerals as little-disturbed or as remnant inclusions (Figs. 10, 11). The barite shows a pronounced tendency to clear itself of included matter; but the invaded materials are not removed with equal ease; and, whereas the quartzose host may be eliminated completely, the specularite and associated minerals may remain intact and give the impression that they, rather than the barite, are doing the replacing (Fig. 10). The specularite and biotite seem most resistant; but the thorite and monazite, unless protected by the specularite, may show loss. The barite is in turn penetrated by aggregates of feldspar, calcite, and quartz, and may itself be largely eliminated (Figs. 10, 12).

At the Lucky Horseshoe, the formation of scattered barite aggregates has given some of the mineralized phyllitic zone a spotted, strikingly porphyroblastic appearance.

Feldspar, like the barite, is also generally indicative of thorite mineralization. Because of its relatively easy recognition, it has considerable value as an indicator mineral. Its reddish or pinkish coloration makes it easy to spot but does not safely distinguish it from some of the quartz, which in places is also reddish from included hematite and partly decomposed thorite. The feldspar grains are individually small and can be discerned only with the microscope, but their massive aggregates are conspicuous to the eye. Such aggregates form more or less discontinuous bands, streaks, and irregular masses scattered here and there through the deposits. The feldspar is not abundantly distributed but is present in small but variable amounts in nearly every mineralized shear or fracture zone.

The feldspar is represented by *sodic oligoclase* and *albite* and by less abundant *microcline.* The albite-oligoclase grains are generally littered with minute inclusions (Figs. 7, 8). The grains have indistinct boundaries and generally poorly developed albite twinning. The microcline grains are commonly clear and display plaid structure. Microcline and the plagioclase feldspars may occur in the same deposit but generally not in contact with each other.

The miscroscope reveals that the feldspar aggregates penetrate into and through the barite as well as through the thorite-monazite-specularite masses (Fig. 12). These aggregates show a tendency to clear themselves of the invaded minerals but locally they may be littered with the included remains

(Fig. 8). Because of this clearing tendency, the feldspar aggregates appear as reddish areas in an otherwise grayish setting and simulate the appearance of breccia fragments cemented by specularite and associated minerals. In some places stranded specularite may remain as relic veinlets in the feldspar. Like the minerals before it, the feldspar is invaded by and is in part retained as remnant or shadowy-like inclusions in the quartz.

Calcite is a rarity in the deposits and its distribution appears to be limited to several deposits along Pattee Creek and to one deposit on Agency Creek. It is relatively abundant in these deposits and forms lenticular seams and pods up to several inches thick. Its absence in other deposits may be more apparent than real because of its ready removal from the weathered exposures.

The calcite is coarsely crystalline and its grains tend to penetrate and engulf the feldspars, barite, and earlier minerals and to retain them as remnant inclusions. This behavior of the calcite is particularly noticeable in the case of the barite (Fig. 10). Included specularite and radioactive minerals may largely escape attack by the calcite and retain their crystal outlines (Figs. 2, 11); but more generally they show evidence of partial to almost complete replacement and remain as remnants (Figs. 10, 11), if not removed altogether. Like all the other minerals that have been described, the calcite has been invaded by quartz.

Pyrite has been observed in only two deposits, both of which are along Agency Creek. One of these is just below the Black Bull fraction; the other is on lower Agency Creek. In the first the pyrite occurs as small, widely scattered crystals in the calcite. In the other, the small grains of pyrite are abundantly disseminated through the more quartzose parts of the deposit. It is possible that much of the hydrous iron oxides in the weathered parts of the deposits elsewhere in the area had their source in pyrite. Its presence in the calcite indicates that it is a late mineral, possibly as late or even later than the quartz.

Quartz, which accompanies the thorite mineralization, is present in variable but mostly small amounts in all deposits but is generally not so conspicuous as the quartz inherited from earlier veins or the country rock. It is always abundant enough to be readily visible.

This quartz is relatively coarse-grained as compared with the quartz inherited from earlier fillings and from the country rock, and is characterized by a pronounced, somewhat wavy strain extinction which here and there bears resemblance to the plaid structure of microcline feldspar. The quartz is commonly darkened by inclusions and in places is nearly black.

Some of the quartz fills fractures in the mineralized rock; but most of it, as revealed by microscopic studies, has permeated or soaked into the mineralized rock without completely destroying the evidence of its invasion. Its grains are commonly strewn with the remains of the earlier minerals (Fig. 6). In its infiltration the quartz has generally been less able to clear itself of the thorite and monazite than of the other minerals; and, hence, microscopic inclusions of the radioactive minerals are fairly common (Fig. 5).

Chalcedony is a mineral of limited distribution and seems to be restricted

to the deposits near the Continental Divide both in Idaho and Montana. It occurs in some abundance at the Cago No. 12, and less abundantly in the deposits along the Divide and in Last-Chance Shady Tree lode in Montana.

The chalcedony can not be positively identified without the microscope, for at least some of the brownish, jasperoid-like material found in many of the deposits is quartz littered with remnants of earlier minerals and their decomposition products.

Some of the chalcedony at the Cago and elsewhere fills or partly fills openings in the coarsely crystalline quartz and some cements small breccias of the quartz.

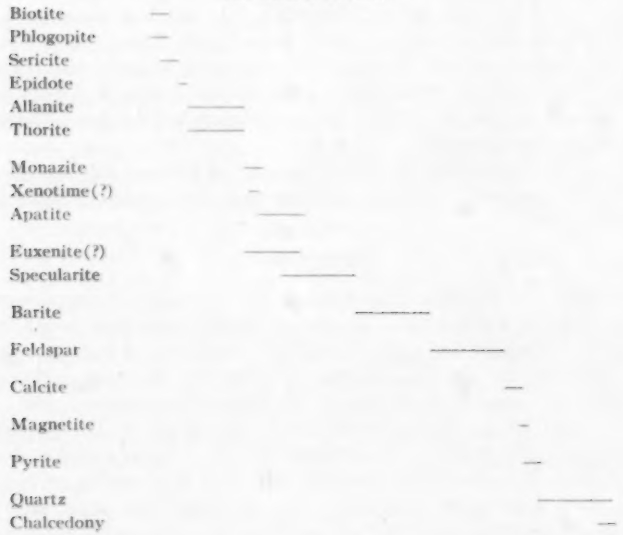
Paragenesis

As brought out in their descriptions, the relations of the minerals are such as to indicate an orderly sequence of development that began with the formation of the micas and ended with the deposition of quartz or of chalcedony. Initiated by the introduction of silicates, the mineralization continued with the successive formation of phosphates, oxides, and sulfates. Silicate formation was then resumed with deposition of the feldspar, followed by carbonates, oxides (?), sulfides, and silica (quartz and chalcedony).

The position of some of the minerals is known only within certain limits; of others, it is fixed more precisely. As the micas are penetrated and in one way or another replaced or partly replaced by all the other minerals, their early formation is unchallenged; but because they were not found together, it is not known which of the micas, the biotite, phlogopite, or sericite, should head the list. Each of these is the first in whichever deposit it may occur. The allanite and thorite pose much the same problem as the micas. Each replaces and is younger than the micas and each in replaced more or less directly by all the other minerals; but owing to differences in geographical distribution, the two do not occur together; and any age or sequential differences cannot be worked out. Both occupy an analogous position in the general sequence. The phosphates also present a problem in the case of the xenotime(?) and monazite. Both are engulfed by aggregates of apatite but whether one is any earlier than the other cannot be worked out on the basis of the existing evidence. They must be very nearly the same age. Except for the magnetite, the oxides are less of a problem, The magnetite does not fit in with the specularite but seems to have a closer tie with the calcite, apparently forming just a little later. Although very closely associated with the thorium and rare-earth minerals, the penetrative and protective habit of the specularite indicates that it formed during the late stages of the thorium and rare earth mineralization, apparently overlapping in places on the intimately contained euxenite (?). The position of the remaining minerals is readily determined. The successive invasions of the deposits by barite, feldspar, calcite, and quartz are well substantiated by litter remnants of all the earlier minerals. The place of the pyrite seems to lie between the calcite and quartz, but actually may be with the quartz.

For easy reference, the mineral succession is tabulated below.

MINERAL SUCCESSION



RARE EARTH ELEMENTS

The rare earth elements in each of the radioactive minerals have not been fully determined. Returns from spectrographic analyses of samples of lode materials sent by owners to commercial analysts merely reveal that the materials contain some rare earths, mainly of the cerium group. Such rare earths have been reported from the allanite-bearing deposit at the Lucky Horseshoe and from several of the thorite-bearing deposits, but whether the analyses reflect the rare-earth content of one of the radioactive minerals or of a combination of such minerals cannot be known until the ores analyzed are examined microscopically. It is hoped that eventually the radioactive minerals may be isolated individually and that each may be investigated for its rare-earth constituents.

The best data to date on the makeup of the rare earths come from two samples of thorite-rich ore from the Cago No. 12 lode that were sent by the owners to the Rare and Precious Metals Experiment Station, U. S. Bureau of Mines, Reno, Nevada, for a breakdown of the various rare-earth elements. One of these samples contained 13.5 percent thoria plus rare-earth oxides and the other contained 9.6 percent of the same constituents. The results of the breakdown into the various elements are shown in Table 1.

Microscopic examination of some of the most highly radioactive material collected later from the same rich concentration proved to be composed of more than half thorite, the remainder of specularite, small amounts of monazite, and sparse xenotime (?). For the most part, the rare earth assemblage must reflect the composition of the thorite.

TABLE 1

	Sample 1 (percent)	Sample 2 (percent)
Total rare earth oxides plus thoria	13.5	9.6
Y_2O_3	2.0	2.3
La_2O_3	3.5	2.9
CeO_2	11.5	10.0
Md_2O_3	15.1	15.0
Sm_2O_3	11.5	16.1
Eu_2O_3	1.3	1.3
Gd_2O_3	4.0	3.7
Er_2O_3	0.6	0.7
Tm_2O_3	3.0	3.3
Yb_2O_3	1.6	1.2
Lu_2O_3	1.3	1.2
ThO_2	43.8	47.3

DISTRIBUTIONAL CHARACTERISTICS OF THE MINERALS

The minerals in these deposits show a generally spotty distribution. They occur irregularly through the broad zones of fractured rock, commonly in greater concentration in the areas of more extensive fracturing. In some deposits the minerals are largely concentrated in thin, lenticular bodies and discontinuous veins up to several feet thick and a few tens of feet long; in other deposits they are distributed among several veins spaced a few feet apart. In other fracture zones the minerals are largely restricted to irregular masses and pockets. Such mineral concentrations mark the areas of high radioactivity; but less intense radioactivity may continue far beyond the borders of these visible concentrations, indicating some mineralization to the very borders of the fracture zones. The minerals need not necessarily be visible. At the Wonder lode the thorite, unrecognizable to the unaided eye, has been deposited in fractures in which virtually no other vein minerals have been deposited. The irregular distribution applies to the individual as well as to the mineral groupings. The spotty character of so much of the mineralization is shown by such minerals as the megascopically visible, specular hematite, feldspar, and late quartz. These generally occur together in variable proportions but any one may overshadow the others locally.

In the quartz and copper veins the introduced minerals are largely confined to irregularly distributed fractures. As the fracturing is so much weaker in these older quartz veins than along the independent zones of shearing in the country rock, only minor amounts of thorite are generally found in the quartz and copper veins.

SIZE AND TENOR OF THE DEPOSITS

The mineralized zones with their sparse to locally rich concentrations of thorite and associated minerals range from less than 1 foot to 50 feet or more wide and up to 2,000 feet long. These zones may show notable concentrations of the radioactive and associated minerals for some tens of feet, excep-

tionally for some hundreds of feet, then the concentrations terminate as the minerals dwindle in quantity and disappear. Such concentrations may range from several to 10 feet or more across, with less extensively mineralized rock extending outward to the walls. Mineralized zones may thus measure up to 40 feet or more across and may continue on strike for some hundreds of feet before the mineralization shows conspicuous signs of weakening.

The tenor of the mineralized rock is as variable as the distribution of the minerals, but the richer concentrations compensate for the parts that are lean, and the deposits may possess satisfactory grades of ore for considerable distances. The largest vein in the area, the Last Chance, on the Montana side of the Divide (Fig. 1), has been traced 1,300 feet on the surface. It ranges from a few inches near its north end to a maximum of 35 feet near the south end, averaging 10 to 15 feet thick for much of the distance and showing a thickness of 20 feet in two drill holes, one 260 feet and the other 290 feet down dip (8, p. 37). Samples of the vein along the surface are reported by Moen (3, p. 21) to contain 0.60 to 3.34 percent thoria and at the 240-foot depth, 0.52 percent thoria. According to Weiss et al. (8, p. 37) samples from the strongly radioactive parts of the vein have assayed as much as 2.1 percent thoria; but they concluded that scattered surface samples, drill-hole data, and geologic interpretation suggest an average grade of 0.15 percent thoria with small amounts of uranium and rare earths.

At the Cago No. 12, which contains one of the richest thorite concentrations in the district, the 10-foot vein has been exposed by cut for nearly 200 feet. A sample taken of the more highly radioactive material in the writer's presence and analyzed at the Mountain Pass laboratory of the Molybdenum Corporation of America contained 14.79 percent combined thoria and rare earth oxides. Another sample of the more siliceous material, perhaps more representative of the deposit as a whole, had 0.7 percent thoria and rare earth oxides. Chemical analyses of selected samples taken by Moen (3, p. 20) disclosed 6.85 percent thoria and 0.147 percent uranium oxide. Underground work in 1959 revealed that the mineralization entered a large quartz body at slight depth and that the grade of ore diminished appreciably.

At the Wonder lode, the upper adit exposed the mineralized fracture zone for 100 feet. The lode there averaged 2½ feet wide and contained 0.75 percent thoria, ranging from 0.05 to 2.66 percent (3, p. 21). In the lower adit the 150-foot length of the lode had an average thickness of 1¾ feet and averaged 0.30 percent thoria, the limits ranging from 0.02 to 0.502 percent thoria.

A sample across 6 feet of the most highly radioactive part of the 40-foot lode on the Black Bull fraction contained 1.22 percent equivalent thoria.

At pointed out by Trites and Tooker (6, p. 169) and later by Sharp and Cavender (5, p. 1555), the thoria content of most of the deposits probably ranges from 0.1 to 2.0 percent and averages somewhat less than 1 percent; but some deposits discovered since then may contain greater concentrations of radioactive minerals than the others and may average even above 1 percent thoria. According to Moen (3, p. 5) the average grade of seven of the deposits is 0.72 percent thoria.

ORIGIN OF THE DEPOSITS

The paragenetic and other relationships indicate that the thorite and associated minerals were introduced into zones of sheared or fractured rock and into reopened quartz and copper veins and the presumption is that the mineral constituents were brought in and deposited by heated solutions derived from deep magmatic sources. Unlike most hydrothermal solutions from which ores are deposited, these were exceptionally enriched in thorium, rare earth elements, phosphorus, iron, barium, calcium, sodium, potassium, sulfur, and silicon, and also in small but significant amounts of columbium, uranium, and other substances. Such a combination of elements is characteristic of the deposits known as carbonatites (4, p. 1537–1556) which differ in substance from the local thorite deposits largely in the presence of abundant carbonates, principally calcite. Such deposits are invariably associated with alkalic igneous rocks and have been formed from carbonatic fluids genetically related to alkalic magmas. Although the deposits in the Lemhi Pass area are not carbonatites, they appear to have had a closely similar history, and to have been formed by hydrothermal solutions, deficient rather than abundantly supplied with carbonates. They have no visible association with alkalic igneous rocks, unless the lamprophyric rocks constitute evidence of such an association. It is probably safe to conclude that the deposits are of hydrothermal origin and that they were formed at relatively high temperatures, at least during earlier stages of mineralization.

As the hot fluids with their variable concentrations of thorium, rare earth, and other constituents moved upward from their magmatic source along the zones made permeable by fracturing, they penetrated the rock and older veins; and, after inducing the formation of some micaceous minerals, they deposited much of their thorium along with the rare earth elements; then in turn, the iron, barium, sodium, potassium, locally calcium, and lastly silicon. Most of the thorium with some of the rare earth elements combined with the silicate radical to form thorite; but at the Lucky Horseshoe the thorium, rare earths, and other elements joined with the silicate radical to form allanite. Thorium and rare earths not entering the thorite and allanite then combined with the phosphate radical to precipitate as monazite and to much more limited extent as xenotime(?). Excess phosphate was taken up by the calcium to form locally abundant apatite. Columbium also claimed its share of the thorium, yttrium, and perhaps other rare earths and uranium and came out as the oxide, euxenite(?), close on the heels of the silicates and phosphates. The precipitation of the thorium and rare earths ended in the oxide stage, apparently just as the iron began to come out as specularite, which brought an end to the economically important phase of the mineralization.

As the heat-losing fluids continued to move along the channelways, the contained barium combined with the sulfate radical to form barite, which was deposited in part at the expense of the earlier minerals. After this the alkalies, sodium and potassium, united with aluminum and the silicate radical to form albite or sodic oligoclase and microcline. Remaining calcium combined locally with what carbonate was present to form calcite. Whatever

iron and sulfur may have remained or may have been present in the solutions precipitated in places as magnetite and as pyrite, although the pyrite may have awaited the deposition of quartz, which terminated the mineralization.

Except for the feldspar, the mineral succession seems to be an orderly one; but, if the physiochemical aspects of the mineralization were better known, the feldspar might be found to be in its proper place for this type of mineralization. The mineral sequence appears to reflect changing thermal as well as chemical conditions during the coarse of mineralization. The micas and the thorium silicates, the phosphates, and the oxides suggest that during early stages the mineralization took place at notably high temperatures or under hypothermal conditions. The succeeding succession of barite, feldspar, calcite, and quartz indicate declining temperatures, although perhaps still within the hypothermal range. The chalcedony may have been introduced some time after the main mineralization in a then much cooler environment.

Until the mineralization is dated radiometrically, the age of the mineralizing solutions cannot be precisely established. Deposits similar to these in the Diamond Creek area 6 to 8 miles north-northwest of Salmon cut a supposed outlier of the Idaho batholith, which locally transgresses late Laramide structural features and which therefore is late Cretaceous or early Tertiary (2, p. 37–40; 85–90). Because the thorite mineralization at both places is virtually identical, that at Lemhi Pass is probably likewise of late Cretaceous or early Tertiary age. That the mineralization can be no younger is demonstrated by the fact that the deposits are older than the cover of Tertiary volcanic rocks.

OUTLOOK

Although the deposits have not been extensively explored, the work done, largely on the surface, has disclosed significant amounts of thorium. Some of the deposits contain several percent thoria and comparable amounts of rare earth oxides; but any sustained operations would have to be based on lower grade ore, most of which would average somewhat less than 1 percent thorium oxide. For economic utilization the ore must be upgraded and this problem is receiving serious attention.

Some promising showings have been found during the recent wave of exploration and the geologic probability that additional thorium occurrences will be found is excellent. Most of the showings are now in the hands of responsible organizations with the financial backing needed to develop the deposits and bring them into production. The largest and most extensively developed deposit with a presently estimated reserve of a million tons of ore, the Last Chance-Shady Tree lode in Beaverhead County, Montana, has been acquired by the Sawyer Petroleum Company. This company has recently announced a "technologic break through" (Eng. Min. Jour., vol. 160, No. 10, Oct., 1959, p. 137) in the reduction of the ore to yield a concentrate containing 35 percent thorium. The Rare Metals Corporation, a subsidiary of El Paso Natural Gas Company, has recently (Mining World, vol. 22, No. 1, Jan., 1960, p. 63) entered into a contract with the Agency Creek Thorium

and Rare Metals Corporation of Salmon, Idaho, for exploration, development, and mining of thorium and rare metals on the 78 claims comprising the Agency Creek property. Some ore from the property was milled during 1959 and expanded production is planned beginning in 1960. A recent merger gives the Nuclear Fuels and Rare Metals Corporation control of some 7,000 acres, chiefly in Lemhi Pass, formerly held by the Idaho Thorium Company, the Salmon Uranium and Development Company, and several other parties as well as ownership of a 100-ton mill that is to be put into operation during 1960. Much surface work and some drilling and underground work have been done at the Lucky Horseshoe by the owner, Fred Guderjohn, Idaho Falls, Idaho. Several cars of allanite-rich ore are stockpiled on the property. During 1959 the Atomic Energy Commission began work on an appraisal of the thorium ore reserve. The Lemhi Pass area has become significantly important, containing one of the major concentrations of thorium presently known in the country.

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OBSERVATIONS ON CATION EXCHANGE IN SOME MANGANESE MINERALS BY ELECTRODIALYSIS[1]

B. L. SREENIVAS AND R. ROY

ABSTRACT

The behavior of cations in some manganese minerals was studied by electrodialysis. Among the common manganese oxide minerals, psilomelane, hollandite, lithiophorite, chalcophanite and hetaerolite showed no change. Cryptomelane (α-MnO_2) shows significant cation exchange, passing through an intermediate contracted cell stage. It finally changes to γ-MnO_2 after a few hours of dialysis. Braunite undergoes remarkable changes appearing to transform into bixbyite.

INTRODUCTION

Ion exchange has been known to occur widely in nature. Most of our understanding of the ion exchange in minerals is derived from observations made on clays, zeolites and synthetic alumino-silicates. Realizing the importance of certain possibly exchangeable cations in manganese minerals, Fleischer and Richmond (4) suggested qualitative chemical tests in addition to X-ray studies for positive identification of manganese minerals. In the literature, association of many elements with the manganese oxide minerals has been attributed to "adsorption" without considering the possibility of ion exchange. However, the importance of such an exchange in artificial preparations of manganese oxides is fully recognized by the battery industries.

Gruner (5) on boiling α-MnO_2 in solutions of silver nitrate, barium chloride, and lead nitrate, noticed that silver ions enter the structure more easily than barium and lead ions. He also came to the following conclusions: 1) part of the K^+ ion is replaced by the new metal, 2) there must be open positions in the structure into which other metal ions can enter, 3) some ions may just be adsorbed. Cole, et al. (3) showed the importance of K^+ ions in the formation of α-MnO_2. McMurdie (6) converted γ-MnO_2 to cryptomelane by autoclaving with saturated NH_4Cl solution. He considered that K^+ or Na^+ was introduced either from the parent material or in the process of manufacture. Fleischer (4) commenting on McMurdie's work, states that the alkali cations of artificial α-MnO_2 were exchangeable when treated with ammonium acetate, and that autoclaving might cause the loosely bound exchangeable cations to migrate into the lattice. Wadsley (8) describes a hydrous manganese oxide of composition $(Na, Mn)Mn_3O_7$ with exchange properties for certain metal ions. Anders and Marie Byström (2) on the basis of crystal structure work showed that α-MnO_2 requires some

[1] Contribution No. 59–88, Department of Geophysics and Geochemistry, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

large ion to prevent the structure from collapsing. Likewise the psilomelane structure accommodates a large ion in a "hole" and it is conceivable that such an ion could be "exchanged."

The present work was designed to check whether some of these 'extra' ions in manganese minerals could be removed by electrodialysis without effecting a structural collapse, and further, if after removal of the original ion other ions could "stably" substitute for it. In addition to electrodialysis standard exchange procedures were also used.

The electrodialysis cell used in the present study is a three-chamber Lucite unit with platinum electrodes. Parchment membranes were used in the early stages and organic resin membranes prepared by the Permutit Company in the later stages. The center compartment containing the mineral

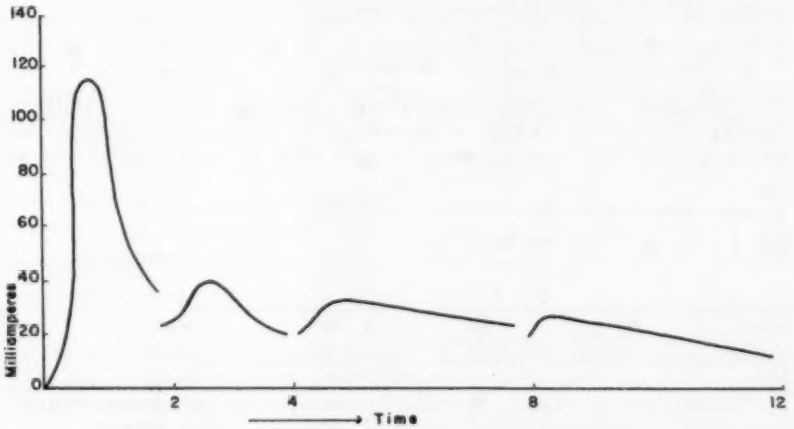

FIG. 1. Current flow in the dialysis cell. (Numbers 2, 4, 8 and 12 indicate the hours at which de-ionized water was changed in the cell.)

is bounded by the semipermeable membranes, the outer compartments contain the anode and cathode respectively in de-ionized water. About two grams of the sample crushed to − 100 mesh were placed in the central compartment of the cell and 650 v D.C. potential was applied across approximately 4 cm. At intervals of two to four hours de-ionized water was added to the cell, after extracting the cathode liquid for analysis. Figure 1 shows the usual pattern of current flow in the dialysis cell for a sample of α-MnO_2.

All the samples were X-rayed before and after each stage of dialysis; patterns were made on a low angle Philips diffractometer using filtered FeK radiation. Some film patterns were also run. X-ray fluorescence and emission spectroscopic methods were used for semi-quantitative determination of the cations. Minerals used in the present study are listed in Table 1. In addition to dialysis, and subsequent to dialysis, attempts were made to

TABLE 1

MANGANESE MINERALS USED

Mineral	*Formula*
Braunite	$3Mn_2O_3 \cdot MnSiO_3$
Chalcophanite	$ZnMn_3O_7 \cdot 3H_2O$
Coronadite	$PbMn_8O_{16}$
Cryptomelane	KMn_8O_{16}
Franklinite	$(Zn \cdot Fe \cdot Mn)O \cdot Fe_2O_3$
Hetaerolite	$ZnMn_2O_4$
Hollandite	$BaMn_8O_{16}$
Lithiophorite	$(Al \cdot Li)MnO_2(OH)_2$
Psilomelane	$(Ba \cdot H_2O)_2 \cdot Mn_5O_{10}$

exchange the cations in the various phases by repeated shaking with concentrated solutions containing the desired ions.

RESULTS

Psilomelane, hollandite, lithiophorite, chalcophanite, and hetaerolite showed essentially no change on electrodialysis. Of these, psilomelane and hollandite may have been expected to yield their Ba^+ and perhaps collapse

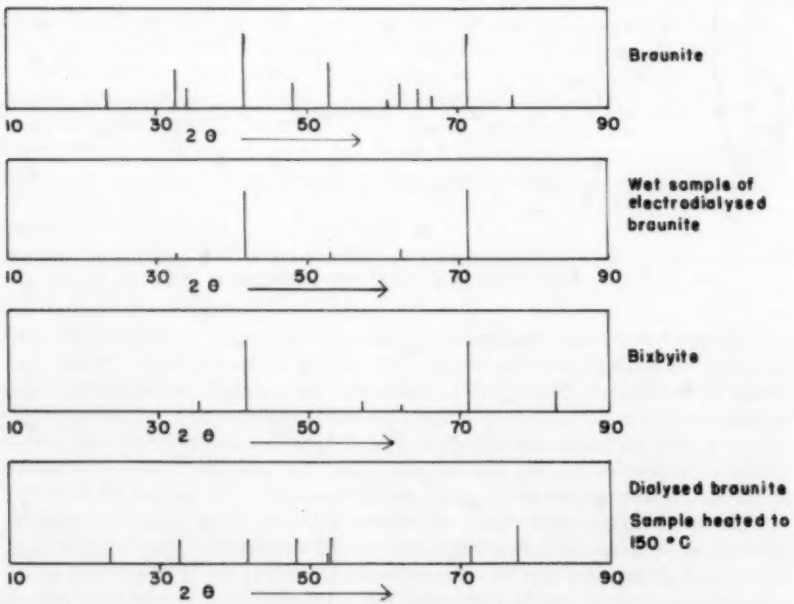

FIG. 2. Intensity patterns of braunite (dialysed—moist and dry) compared with bixbyite.

as a result. This did not happen under the conditions of the experiment used.

Braunite behaved in a rather surprising manner. After the first few hours of dialysis the *cathode* chamber showed the presence of a little silica; continued dialysis resulted in removal of considerable amounts of both silica and manganese from braunite. It was in the examination of the product of this dialysis that considerable interest arose. The sample, if X-rayed while still moist (or at least not intentionally dried), gave a pattern very similar to bixbyite (Mn_2O_3). On drying at 150° C there resulted a pattern similar to the original braunite although distinct from it. This is illustrated in the series of marked intensity changes in Figure 2.

Thus in the braunite pattern the two strongest reflections at approximately 2.70 and 1.66 Å which are also the strong reflections of bixbyite are the only two that survive in the moist sample. All moderate intensity reflections appear to be lost or greatly weakened. On even moderate drying the strong reflections are much weakened and a new intensity pattern with splitting of some peaks appears. The work done so far is insufficient to explain these phenomena. It should be noted that our colleague Prof. A. Muan of the Department of Metallurgy has recent evidence to show that at

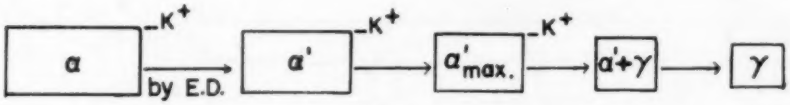

FIG. 3.

high temperatures there is solid solution of (Si^{4+} and Mn^{2+}) in the bixbyite structure. Perhaps the wet sample represents essentially a bixbyite solid solution with Si^{4+} cations removed and charge balance achieved through O^{2-} replacement by $(OH)^-$ giving a structure more similar to bixbyite than the original braunite. The elimination of water on heating may force the ions to a new arrangement.

Franklinite, $(Zn \cdot Fe \cdot Mn)O \cdot Fe_2O_3$ has the spinel structure and it was surprising to find that appreciable quantities of first, Zn, and then Fe (with some Mn) were removed by dialysis resulting in a slightly modified structure and altered intensity distribution. In neither of these last cases is it likely that exchange or cation leaching was the only effect; oxidation reactions perhaps played an important part although this may be consequent on partial destruction of the original structure and subsequent oxidation by water under ambient conditions.

The most interesting result is achieved with cryptomelane. Cryptomelane can reversibly lose part of its K^+ and form a maximum-distorted cryptomelane phase (α^1). The 'a' axis contracts from 9.82 to 8.78 Å while the 'c' axis contracts from 2.83 to 2.77 Å. At this stage analysis shows that approximately half the potassium has been extracted. On further dialysis the cryptomelane structure is destroyed and γ starts to appear, and in a

matter of about 15–20 hours only γ is left. These reactions are summarized in the schematic form Figure 3.

Natural cryptomelanes, due probably to their better crystallinity tend to lose their K^+ more slowly than the synthetic phase, but go through the same process.

An attempt was also made to check which cations can substitute for K^+ by treating the α^1 phase with the halide solutions of various cations. The resulting powder patterns are shown in Figure 4.

Most of the solutions appeared to cause unexpectedly severe changes. With cuprous ions a reasonably complete α is restored and it is possible that Cu^{1+} replaces K^{1+}. The Cr^{3+} showed a substantially analogous α which may

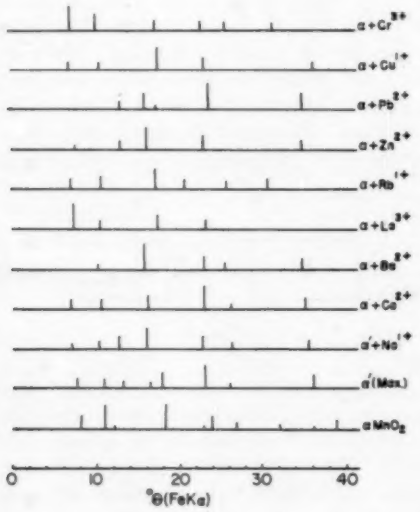

FIG. 4.

be due to replacement of part of the Mn^{4+} by Cr^{3+} giving internal compensation for the loss of K^+ in the α^1 phase.

CONCLUSION

Cryptomelane can be converted in a few hours by electrodialysis into γ-MnO_2. It passes through an intermediate stage (α^1), which represents a maximum distortion of the structure caused by loss of approximately 50% of its K^+. Among the common crystalline manganese oxides, only in cryptomelane does cation exchange appear to be of any significance. Braunite on electrodialysis loses both silica and manganese ions and gives a phase which when wet gives a bixbyite-like pattern.

ACKNOWLEDGMENT

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DETERMINATION OF APPARENT ANGLES OF INCLINED LINEAR ELEMENTS

JOHN C. HAGEN

ARSTRACT

The apparent plunges of inclined drill holes and linear geological structures which perforate or approach a vertical cross-section obliquely should be shown accurately for correct data representation. Much time can be saved by using a graph or a slide-rule computer to determine the apparent angles of linear elements. The two mapping aids are based on the relationship $\tan\gamma = \tan\alpha/\cos\beta$ where is the angle of plunge, is the angle of convergence, and is the apparent inclination.

INTRODUCTION

THE determination of the apparent inclination of a line when that line is projected to a vertical plane not parallel to its bearing is an important application of descriptive geometry useful to geologists and mining engineers in plotting inclined diamond drill holes and linear geological structures on oblique cross-sections. It is common knowledge that the inclination of a dipping plane reaches its maximum angle, the true dip, when projected to a vertical plane striking at right angles to the inclined plane and its minimum angle, zero dip, when projected to a vertical plane having the same strike. This differs from the apparent inclination of a line plunging one degree or more which attains its maximum inclination i.e. 90 degrees when projected to a vertical plane striking at right angles to the bearing of the line and its minimum angle when projected to a vertical plane striking parallel to its bearing which, of course, is its true plunge.

APPLICATION

In the analysis and solution of many structural geology problems and in proper mapping procedure, the apparent angles of inclined drill holes or linear structures that perforate or approach a vertical cross-section obliquely should be shown accurately on the section for correct data representation.

In probing and delineating irregularly shaped orebodies for development or exploration purposes, underground diamond drilling may be done at various inclinations and bearings from scattered headings in order to penetrate target areas economically and efficiently. As a result, much of the section mapping time is spent determining the apparent plunges of holes and plotting these angles either at the "pierce points" where the holes perforate one or more cross-sections that transect the target or at the projected collars or toes of holes that approach or lie relatively close to a cross-section.

Similarly, the apparent plunges of mapped linear structures such as pencil-like orebodies or ore shoots, texture lineations, and fold axes are posted on

a converging cross-section when the structure either penetrates it or is projected to the cross-section through a short distance.

METHOD

Although basic methods employing trigonometry, geometry, and graphics, as well as stereographic projection (1), can be used to determine the apparent dip of a known line when projected to a given vertical plane, the writer has found that much time can be saved by using a graph or slide-rule computer that read angles to the accuracy required for good mapping procedure (Figs. 2, 3). Both the graph and the computer have been used

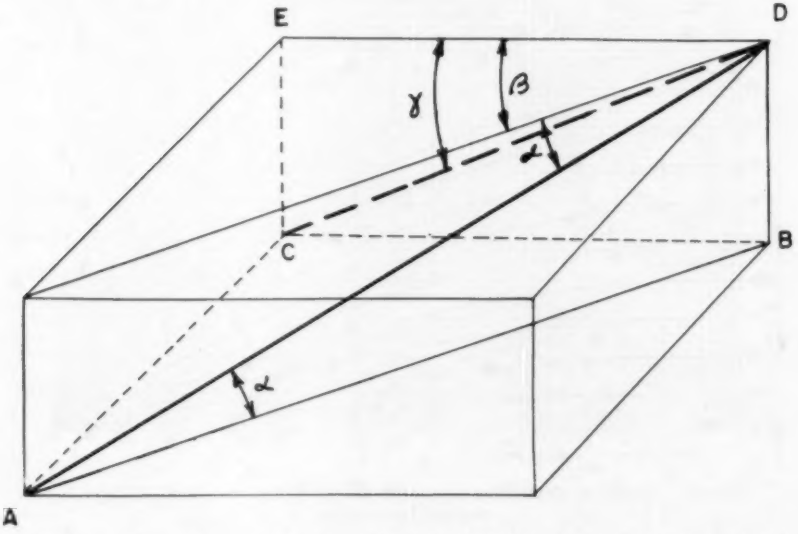

FIG. 1. Block diagram showing the relationship between inclination of line (α), the apparent angle of line (γ) on plane of projection ($CEDB$), and convergence angle (β).

profitably for posting data on cross-sections at Iron Mountain Mine, Missouri where multi-angled drilling on radial cross-sections is necessary, and at the Raposos and Morro Velho mines near Nova Lima, Brazil where pencil-like ore shoots are localized in plunging folds.

Both the chart and the slide rule are based on the trigonometric relationship:

$$\tan \gamma = \frac{\tan \alpha}{\cos \beta} \qquad (1)$$

which gives the apparent angle (γ) in terms of the plunge (α) and the convergence angle (β), the angle between the bearing of the line and the

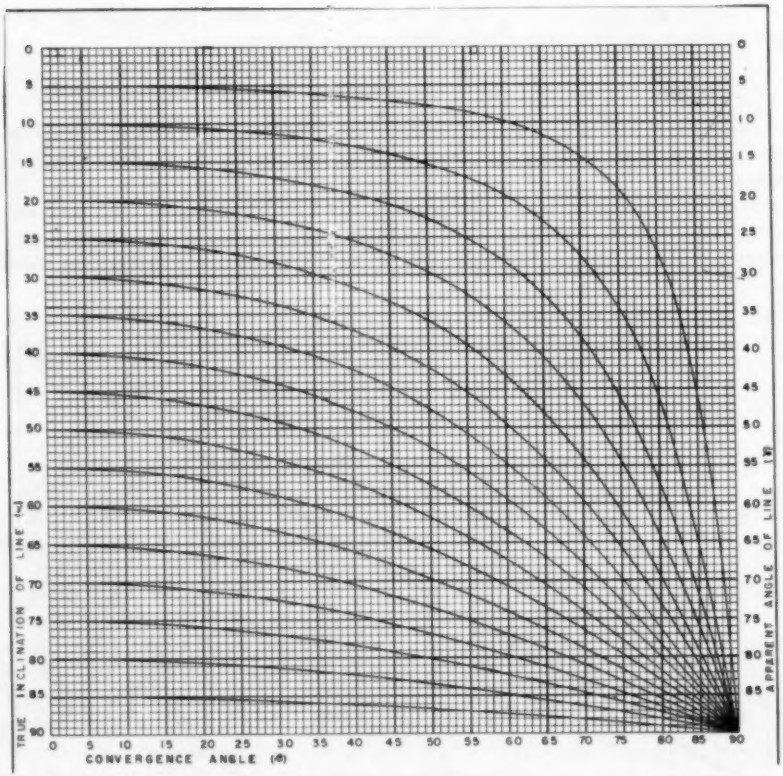

FIG. 2. Graph to determine apparent angle of line on vertical plane by normal projection.

strike of the vertical plane of projection (2). The equation is derived as follows:

In Figure 1,

α = true inclination or plunge
β = convergence angle
γ = apparent inclination
AD = line in space
$DECB$ = plane of projection
DC = line projected on $DECB$.

In $\triangle BCD$, $$\tan \gamma = DB/BC. \tag{2}$$

In $\triangle ABD$, $$DB = DA \sin \alpha, \tag{3}$$

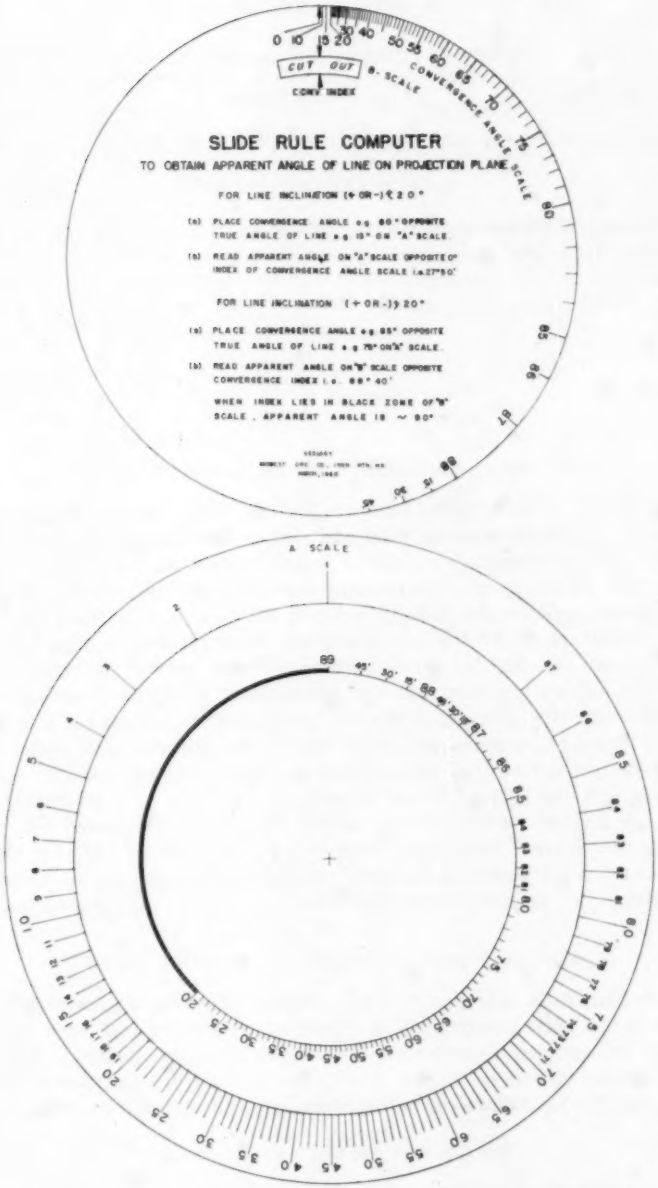
CUT OUT
CONV INDEX
B- SCALE
CONVERGENCE ANGLE SCALE
SLIDE RULE COMPUTER
TO OBTAIN APPARENT ANGLE OF LINE ON PROJECTION PLANE
FOR LINE INCLINATION (+ OR -) ≤ 20°
(a) PLACE CONVERGENCE ANGLE e.g. 60° OPPOSITE TRUE ANGLE OF LINE e.g. 15° ON "A" SCALE.
(b) READ APPARENT ANGLE ON "A" SCALE OPPOSITE 0° INDEX OF CONVERGENCE ANGLE SCALE i.e. 27°50'
FOR LINE INCLINATION (+ OR -) > 20°
(a) PLACE CONVERGENCE ANGLE e.g. 65° OPPOSITE TRUE ANGLE OF LINE e.g. 75° ON "A" SCALE.
(b) READ APPARENT ANGLE ON "B" SCALE OPPOSITE CONVERGENCE INDEX i.e. 68° 40'
WHEN INDEX LIES IN BLACK ZONE OF "B" SCALE, APPARENT ANGLE IS ~ 90°
A SCALE

FIG. 3. Slide rule computer for determining apparent angles of lines. Cut out both circular faces and mount each on cardboard. Cut out "window" for inner "B" scale as noted and attach smaller on top of larger circle at the center positions. Instructions for use of the computer are printed on the smaller or upper dial face.

and $$BA = DA \cos \alpha. \tag{4}$$

In $\triangle ABC$, $$BC = BA \cos \beta. \tag{5}$$

Substituting $DA \cos \alpha$ from equation (4) for BA in (5),

$$BC = DA \cos \alpha \cos \beta. \tag{6}$$

Substituting $DA \cos \alpha \cos \beta$ from equation (6) for BC and $DA \sin \alpha$ from equation (3) for DB in equation (2),

$$\tan \gamma = \frac{DA \sin \alpha}{DA \cos \alpha \cos \beta} = \frac{\sin \alpha}{\cos \alpha} \cdot \frac{1}{\cos \beta}$$

or

$$\tan \gamma = \frac{\tan \alpha}{\cos \beta}. \tag{1}$$

GRAPHICAL DETERMINATION OF APPARENT ANGLE

The results of substituting numbers for (α) and (β) and solving for (γ) in equation (1) have been compiled and plotted in the graph shown in Figure 2. The true inclination or plunge of a line is read on the ordinate scale at the left side of the graph, the convergence angle on and abscissa scale, and the apparent angle on the ordinate scale at the right side of the graph. The curves, which are shown for 5-angle increments, represent the true inclination or plunge of the line. Intermediate angles are applied by interpolation. Thus, one follows a curved line (or interpolated line), representing the inclination of the line, starting at the left ordinate scale, and at the intersection point of it and the convergence angle read at the abscissa scale, one can determine the respective apparent angle at the right ordinate scale.

The graph can be read to an accuracy of one-third of a degree for most angle combinations, which is well within the accuracy required for proper mapping procedure. Moreover it can be used also for determining the true inclination of a line knowing the apparent and convergence angles, a case that often arises when mapping linear features off section in underground headings.

SLIDE-RULE DETERMINATION OF APPARENT ANGLE

A circular slide rule designed to compute apparent angles rapidly and accurately has been constructed in a manner similar to that used by Satin (2) who has adopted a similar aid for computing apparent dips. The slide-rule computer shown in Figure 3 was constructed from equation (1) by substituting the logarithms of the functions into the equation to obtain:

$$\log \tan \gamma = \log \tan \alpha - \log \cos \beta \tag{7}$$

By plotting the logarithms of the tangent functions on one linear scale and the cosine functions on another, one obtains a slide rule for solving equation (7). Figure 3 is a circular modification of the slide rule with the direc-

tions for use printed on the face of the convergence scale dial. The "A" and "B" scales are similar tangent scales which are used here to avoid overlap of the inner circle values on the outer and thus prevent any confusion in the reading of apparent angles greater than 87°.

ACKNOWLEDGMENTS

The writer is indebted to The Hanna Mining Company for permission to publish this paper and wishes to thank Dr. F. M. Chace for reading the manuscript. He is grateful to Mr. V. M. Mejia and Mr. J. E. Murphy, geologists of Midwest Ore Company for assisting with the computations and in the construction of the slide-rule computer.

GEOLOGY DEPARTMENT,
MIDWEST ORE CO.,
IRON MOUNTAIN, MO.,
April 11, 1960

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Economic Geology
Vol. 56, 1961, p. 210

B. S. BUTLER

Bert S. Butler, an Associate Editor of this JOURNAL for twenty-eight years, and former Professor and Head of the University of Arizona's Department of Geology and Mineralogy in the College of Mines, died in Tucson, Arizona, November 13, in his 83rd year.

Dr. Butler was born in Gainsville, N. Y., and graduated from Cornell in 1905, taking his Master's degree there in 1907. In 1928 he was awarded an honorary Doctor of Science degree by the Colorado School of Mines. He joined the U. S. Geological Survey in 1907 and remained with it until 1920 when he became head of special survey for the Calumet and Hecla Copper Co., rejoining the Survey in 1924. In 1928 he was made Professor of Geology at the University of Arizona, later becoming Head of the Department. He remained at the University for the rest of his life. There he was an inspirational teacher and was responsible for much of the outstanding development of the Department of Geology. He was also one of the builders of the present program of the University. He was President of the Society of Economic Geologists in 1932, and in 1947 he was awarded the Society's R.A.F. Penmore Gold Medal for his outstanding original contributions to the science of Geology.

His many publications in the field of geology are well known among geologists; some of them remain as classics. He was a voluminous contributor to the pages of this JOURNAL through which his work became widely and favorably known throughout the world. In his 28 years of service as Associate Editor of this JOURNAL he was ever ready to be of assistance, and his sound criticisms helped guide its editorial procedures.

His kindly disposition; his sense of fairness; and his cordial friendship will be remembered by all who were privileged to know him.

A. M. B.

Economic Geology
Vol. 56, 1961, pp. 211–214

SCIENTIFIC COMMUNICATIONS

THE DETECTION OF RADIO-ACTIVE MINERALS WITH INFRARED AERIAL PHOTOGRAPHY

ERHARD M. WINKLER AND BARRY VOIGHT

Infrared films have been subjected to extensive tests regarding their use in such fields as forestry, water resources management, geology, and sometimes for planimetric mapping. Laylander (2, 3, 4), has applied different kinds of films, including infrared films, in the field of mineral exploration. He reports (2, p. 855): "There is a great field of potential research in study of areas by means of special color films and filter combinations, in determining non-visible changes in rock colors, related either to hydrothermal alteration or facies changes." Laylander continues: "On the Colorado Plateau a color photogeologic study of about 2,000 sq. miles of the uranium producing areas indicated that there were generally subtle alterations of the rocks reflecting ore zones largely overlooked by ground studies. In the Big Indian area, for example, infrared color film with a special filter combination showed a change from reddish to a yellowish color in the Chinle formation near ore zones, which could not be seen either on black and white film or visually."

The film mentioned above is known as Camouflage-Detection film and is essentially Eastman-Kodak's Aero-Ektachrome film with an infrared sensitive layer (infra-red color film). Objects highly reflective are registered in a visible red, e.g.: healthy foliage appears to be red, bare soils brown or green. This reversal of color offers a peculiar color pattern on an airphoto taken with the infra-red color film.

Laylander's comments quoted above made the authors wonder if radiation from a moderately radio-active source would influence film emulsions, especially under conditions of aerial photography. In order to achieve objective information the authors exposed a number of commercial films to radio-active sources of different intensities, both natural and fission products. The experiments were as follows:

The following ore minerals from the local Geology Department's mineral collection at Notre Dame were laid out on heavy white drafting paper and photographed with a nine by twelve cm sheet film Voigtlaender view camera: botryoidal pitchblende, Copper King Mine, Larimer County, Colo.; pitchblende with carnotite and autunnite, Great Slave Lake, Canada; carnotite in sandstone, Colorado Plateau, Utah; U_3O_8 concentrate, Blind River,

Ontario. Three pictures were taken for each experiment both in subdued light and in total darkness at about 24 inches distance from object to film; another set of exposures was made with mineral specimens fully covered with the same white heavy drafting paper that underlies the specimens. The following film-filter combination was used: Kodak Super XX sheet film, ASA 100, no filters; Aerographic Infrared film (black and white), ASA 100, with Wratten No. 12 filter (medium yellow, minus blue); Aerographic Infrared film (black and white), Wratten 89B filter (deep red, nearly opaque to the human eye); Aero-Ektachrome film, ASA 40, 1 color correction filter; Aero-Ektachrome Camouflage Detection film (infra-red color), ASA 32, no filter; Aero-Ektachrome Camouflage Detection film (infra-red color), ASA 32, Wratten No. 15 (G) filter, as suggested by the manufacturer.

Photographs were taken in subdued daylight according to the indicated exposure settings. Those pictures taken in total darkness were exposed one and five minutes each. None of the films showed unusual shadows of discoloring upon critical examination. After the specimens failed to bring any results a much stronger radio-active source was applied. This source was 5 mg of radium, which corresponds to 5 millicuries. This is a much greater intensity than any radiation emitted by even large scale natural uranium deposits. Even this high powered source of radiation did not affect the film emulsions with the normal exposures.

Although the distance from the camera to the source was just a few feet as compared with the altitudes common in aerial photographic flights no effect of any radio-active source material could be observed nor should be expected, as the intensity of radio-active emission depends upon the inverse square of the distance. This fact proves the apparent inability of radio-active sources to affect any one aerial film, neither directly by the bombardment of the film emulsion by radiation nor indirectly by the heat freed during radio-active decomposition. Thus the subtle alterations reported by Laylander were due to a cause other than radio-active emission.

The authors realize the possibility that special infra-red heat sensor cameras may pick up the heat from low-flight altitudes. However, if workable, the authors do not consider this method practical as airborne scintillometers probably do the job better and cheaper than infra-red sensors. A combination of the use of infra-red sensor cameras in conjunction with airborne scintillometers may be of interest for future exploration programs.

The investigations were partially sponsored by the Office of Naval Research, Geography Branch. (Nonr-1623(08))

UNIVERSITY OF NOTRE DAME,
NOTRE DAME, INDIANA,
Oct. 28, 1960

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PLACER CASSITERITE OF THE "MANLEY TIN BELT," ALASKA

KIRK W. STANLEY

Placer cassiterite is a common accessory mineral in certain gold placer districts of interior Alaska. The early idea that the cassiterite was possibly authigenic and equivalent to the chemically precipitated wood tin, as described by Newhouse and Buerger (1), from certain placers in the western U. S. was promoted by the failure to locate a local lode source. If the cassiterite is truly detrital, a local lode source could be expected, but if a chemical precipitate, such a source would not be promising. Thus the purpose of this study was an attempt to establish whether or not the stream tin from one well known placer district was a product of mechanical disintegration of a concealed lode or a chemical precipitate from colloidal solutions.

With these questions in mind the writer, while a graduate student at Montana School of Mines, obtained several pounds of placer cassiterite from the Strandberg Mining Company's gold placer operations at Toffa and Eureka Creeks. Both creeks are within the so called "Manley Tin Belt."

This area is located adjacent to the Tanana River approximately 100 miles west of Fairbanks and near its confluence of the Yukon River. The Manley district has produced placer gold for well over 40 years and is one of the better known districts in which placer cassiterite is associated with the auriferous gravels. The geology of the Manley area consists of Paleozoic and Mesozoic sediments intruded and metamorphosed by granitic plutons of Tertiary age (2). Slate and argillite predominate, but indurated limestone is known in the area.

Because cassiterite and associated minerals are sufficiently transparent to be readily adaptable to optical studies several dozen thin sections, and a lesser number of polished-thin sections, were prepared. In addition to the optical work, chemical and spectrographic analyses were performed.

The cassiterite specimens are similar in physical characteristics. All are dark brown, well rounded smooth pebbles, but somewhat flattened or elongated and vary in size from ½ inch to 1 inch in diameter.

The cassiterite, as viewed by plain light in thin sections using a blue filter is colorless, but light yellow with a reddish tinge when viewed by unfiltered light. Zonal arrangement of colors was not observed and pleochroic haloes are rare. The form of the cassiterite crystals is predominantly subhedral, but euhedral forms are common. Twinning is common and recognized by extinction between crossed nicols.

The principal matrix mineral is quartz, and its micro-brecciated habit and characteristic wavy extension indicates a vein origin. The relationship of quartz to cassiterite is one of intergrowth suggesting the quartz is earlier. Chalcedony and opal are absent. Topaz, although not common, was noted in all specimens and generally as small inclusions in the quartz. Scheelite was noted in several specimens, as was fluorite. The boundary relationship of cassiterite and scheelite suggested contemporaneous development. Tour-

maline, reported by Waters (3), was not observed. Hematite and magnetite were noted in all specimens.

Inclusions within the cassiterite were noted in approximately half of the specimens examined. None of the inclusions transgressed crystal boundaries and thus are considered primary in the sense that they were formed at the time of crystal development.

Twinning indicates the cassiterite is not of colloidal origin. The colloidal structure, described by Newhouse et al. (1) as occurring in what he terms "wood tin," is not present, nor were color banding or contraction cracks noted.

The optical studies strongly suggest the cassiterite and associated minerals are of igneous origin and a product of mechanical disintegration of a cassiterite-bearing lode. The mineral, therefore, should be referred to simply as placer cassiterite rather than as "wood tin."

The problem of possible source is certainly not resolvable by simple optical and chemical analysis. Nevertheless, certain inferences are possible in regard to the type of environment—whether vein, contact, pegmatite or flow —from which the cassiterite may have originated and to which prospecting may be directed in the "Manley Tin Belt."

The absence of sulfides in the specimens, although pyrite does occur in the concentrates, suggests the tin is not a product of local sulfide-bearing veins or a derivative of a volcanic flow.

Although tantalum was noted in analysis, columbium was not, nor was beryllium or any of the rare earths; thus a pegmatite source is unlikely.

On the other hand, the association of scheelite, together with the occurrence of garnet, zircon, epidote, and the abundant quantities of magnetite in the concentrates, suggests the possibility of a limestone contact deposit.

The mineralogic evidence, although incomplete, suggests the placer cassiterite was derived from a lode source such as a contact deposit. Deposits of this type are commonly associated with igneous intrusion into limestone. Future exploration for cassiterite lodes in this area should consider carefully all limestone-granitic contacts and prospecting for the contacts may be facilitated by utilizing the relative abundance of the common contact-metamorphic minerals.

ANCHORAGE, ALASKA,
Oct. 21, 1960

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Economic Geology
Vol. 56, 1961, pp. 215–218

DISCUSSIONS

LEAD ISOTOPES IN ORES AND ROCKS OF BUTTE, MONTANA

Sir: The hypothesis presented for the origin of the Butte ore deposits by Murthy and Patterson (in this number) is contradictory to the general hypothesis developed through intensive long-continued geologic study of the Butte district. Butte is a classic hydrothermal ore deposit, studies of which have had a strong influence on the thinking of economic geologists throughout the world. For this reason hypotheses as to its genesis must be developed with more than ordinary care.

The preliminary nature of the data of Murthy and Patterson must be re-emphasized, particularly the data fixing the isotopic composition of the Butte quartz monzonite. They take the isotopic composition of the lead from the quartz of sample S-1 as representative of the whole quartz monzonite mass and indeed, by inference, this composition is extended to the four or more other rock types of the Boulder Batholith described by Knopf (1). The additional extensive work planned by Murthy and Patterson may demonstrate whether or not the lead of sample S-1 is actually representative. Of especial importance to theories of ore-fluid genesis are determinations of the lead composition of batholith-related rocks such as the aplites, alaskites, and pegmatites of the Butte quartz monzonite and the pre-ore quartz porphyries, the post-ore rhyolites, and the late basic dikes of the area.

Murthy's and Patterson's data on the lead isotope compositions of the ores, the pegmatites, and the quartz monzonite are crucial to interpretation of genetic relationships in the Butte district. Neglecting the possibilities of mineralogic lead isotope fractionation (2, 3, 4) for the purposes of this discussion, as do Murthy and Patterson, the ore mineral data in question form a cluster (Murthy and Patterson, Fig. 1). The two pegmatite K-feldspar isotope compositions fall within this cluster, as does one quartz monzonite K-feldspar, while quartz and K-feldspar from another quartz monzonite specimen is Pb^{206} enriched and falls outside the cluster. Murthy and Patterson discard the feldspar lead data because of geologic lead contamination. They state that ". . . all of the feldspar minerals contained significant amounts of a dusty, opaque material which we believe is an alteration product of the feldspar." We have observed "dusty, opaque material" in the K-feldspar in all Boulder Batholith rocks so far studied in this laboratory. We are inclined to view the slight cloudiness of the K-feldspars as either a primary or at most a deuteric feature. At moderate magnifications these feldspars are essentially clear and we believe that most petrographers would consider them to be very weakly altered or fresh. Certainly

there is no clear spatial relationship between the distribution of this feature and hydrothermal alteration. With this in mind, the isotopic similarity of ore minerals and pegmatite K-feldspar is of particular significance. If S-1 quartz lead validly represents the Butte quartz monzonite, and if the pegmatite K-feldspars are in fact uncontaminated, these pegmatites must be genetically more closely related to ore than to their host rock.

Murthy and Patterson have based their statement ". . . the available isotopic evidence constitutes a valid and serious argument against the suggestion that the ores were derived by differentiation and concentration in the late stage fluids of a magma." on several assumptions regarding the geologic behavior of lead isotopes. The most important of these assumptions is that the Boulder Batholith is isotopically homogeneous. This assumption and the definition of a batholith are critical to the interpretation of the above quotation.

If a batholith be defined as essentially a two dimensional mass, the third dimension being confined to moderate depths, as do Murthy and Patterson (personal communication), serious restrictions are placed on the modes of genesis of hydrothermal solutions from a batholith. The above restrictions are removed if a batholith be defined as a mass of much greater vertical extent including, as do Grout (5) and Daly, all those materials incorporated into it or produced by it in its formation, emplacement, and solidification.

With the batholithic model extending to greater depths, petrological and chemical heterogeneities are expectable. Thermal and pressure gradients imposed on the system either allow or preclude mass convection depending on their relative magnitudes. Thus the heterogeneous mass resulting from fractional crystallization may or may not be isotopically homogeneous. The "several non-shallow locations" of Murthy and Patterson wherein ore leads are supposed to have been concentrated could in this way be no more than inherited isotopic heterogeneities in the batholith whether resulting from incorporation of old sediments or from the differences in isotopic composition between the upper and lower crustal rocks encountered.

In short, the unconventional hypothesis proposed by Murthy and Patterson may simply rest on the definition of a batholith and does not necessarily depart from the classic concept of the genesis of hydrothermal epigenetic ore deposits of the Butte type, a pertinent portion of which was expressed by Waldemar Lindgren (6) as follows: "It is maintained that the ore deposits (of the western United States) originated in part from cupolas of batholiths, in part from the deeper regions of the batholiths, in part from the magma basins whence the batholiths were slowly pressed upwards. But in part they also came from the still deeper magma basins where the effusive rocks were differentiated. . . ."

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Lester G. Zeihen

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The Anaconda Co.,
Butte, Montana,
July 27, 1960

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LEAD ISOTOPES IN ORES AND ROCKS OF BUTTE, MONTANA

Sir: With reference to the discussion of our paper, "Lead Isotopes in Ores and Rocks of Butte, Montana," by Grunig et al., we would like to point out the following:

The pertinent aspect of the alteration of feldspars is that they contain a phase that probably had a genesis more complex than quartz and for this reason are suspect since the formation of this phase may have been contemporaneous with ore deposition. To say that the occurrence of this phase is universal is not pertinent by itself, since it may only characterize an event that is in most cases benign and should only be considered when ore deposition occurs in the vicinity. Even if the formation of this phase preceded ore deposition, its presence would still make the minerals suspect because they may serve as locii highly susceptible to subsequent contamination effects within the ore zone, and this includes ground water circulation.

Quoting us (by personal communication) as believing "a batholith is essentially a two dimensional mass, the third dimension being confined to moderate depths" is apt to convey the wrong meaning. We were referring to that part of the batholith concerned by direct observation. A more explicit statement already exists in the text of our paper. We have considered two possibilities—batholiths originating from lower crustal sources or by large scale melting of sedimentary rock complexes, and in either case we have discussed as to what should be the expected lead isotope picture. The reasons for our assumption that S-I quartz monzonite lead is representative of the igneous rocks are adequately discussed in the paper.

Grunig et al. have brought up a mostly semantic point. They would like to call our "several non-shallow locations" the "deep sources of the batholith." We can in no way test this at present and we were content to say that they were just "several non-shallow locations" which should have certain characteristics in their Pb and U relations. One can speculate on the nature of these relations. For example, there is evidence for believing that the U^{238}/Pb^{204} ratio decreases with depth in the continental crust. At any given location, lead in the entire vertical section may be isotopically homogenized by periodic orogeny. During long periods of quiescence the lead in each substrate may evolve isotopically in different ways until homogenized by a succeeding orogeny. The Butte ores could very well have been derived from

a basic substrate formed 1.5 billion years ago with a $U^{238}/Pb^{204}{}_{T=0}$ is equal to 7. The batholith was emplaced (containing the normal homogeneous mixture of cell leads) and in the dying stages incorporated on a local scale some base metals from this laterally adjacent basic substrate. If, however, the event of first concentration of these base metals was catastrophic and the U^{238}/Pb^{204} ratio was zero, as for example in the case of a base metal mineralization in a uranium free environment, the time of their first differentiation would have occurred 400 m. y. ago. No unique statement can be made about the time of this first differentiation and the U^{238}/Pb^{204} ratios of the system. We mentioned the latter event in our paper because it is the simplest, but we regard the former event as equally or even more probable.

The most important information brought out by our data is that the ores were not related to the associated igneous rocks by a simple differentiation process in one magma. Notwithstanding the statement of Grunig et al., we maintain that this view departs from the classical concepts of hydrothermal genesis of Butte ores. We refer the reader to the extensive literature on Butte, wherein a close genetic relationship between these ores and associated rocks has been emphasized.

It is an admirable idea to follow the footsteps of the great, but their quotation of Waldemar Lindgren on the origin of ore deposits of Western U. S. is not a point of debate now. We are only interested in the new isotopic data and the extent of our present work only concerns Butte. Our discussion and interpretation of these new data, likewise, is limited to Butte and not to the ore deposits of the Western U. S.

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and

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Sept. 15, 1960

Economic Geology
Vol. 56, 1961, p. 219–235

REVIEWS

Geology of Ore Deposits. (Geologiya Rudnykh Mestorozhdenii.) Academy of Sciences of the USSR. January–February, 1959; Vol. 1, No. 1 [1] (in Russian).

Academician A. G. Betekhtin is editor-in-chief of this new journal. The general program of the journal consists in publishing articles on (1) problems of regularities in mineralization processes, and distribution of ore deposits in ore-bearing regions, especially within metallogenic provinces, as well as geological structures of ore fields [2] and separate deposits; (2) theoretical problems in studying ore deposits; (3) problems of elaboration of prospecting and exploration methods, and methods of studying ore deposits; (4) results of mineralogical investigation of ores; (5) results of experiments on the conditions of ore-forming processes; (6) review of foreign achievements in the geology of ore deposits. *Geology of Ore Deposits* is the Russian counterpart of ECONOMIC GEOLOGY. The project of reviewing the journal is undertaken to inform English-speaking geologists about theoretical and practical aspects of the geology of ore deposits in the Soviet Union.

A. G. Betekhtin: Behavior of Radioactive Elements During the Processes of Formation of Endogenous Deposits (Pp. 5–24).

Major geochemical features of radon, radium, thorium, and uranium (U^{4+} and U^{6+}), and the isomorphism of the last three with other chemical elements are summarized, with emphasis on uranium, its affinity to oxygen, and study of uranium minerals. In endogenous radioactive deposits uranium and thorium are present mainly in the form of admixtures in complex oxides of titanite-niobate-tantalate type. These deposits are represented by magmatic deposits of alkaline granites, nepheline syenites, pegmatites, skarn deposits affiliated with massifs of alkaline syenites, and some high-temperature hydrothermal veins. Hydrothermal deposits formed under near-surface conditions are of major interest. However, their reserves are not as high as those of the sedimentary uranium deposits.

The general classification of endogenous uranium deposits is suggested as follows: I. Magmatic deposits: (1) in alkaline granites; (2) in nepheline syenite. II. Pegmatite deposits: (1) in granite pegmatites; (2) in nepheline syenite pegmatites and syenite pegmatites. III. Skarn deposits (no deposits of economic value have been so far discovered). IV. Hydrothermal deposits: (1) high-temperature deposits, mainly uranium- and thorium-bearing; (2) mesothermal and epithermal deposits: (a) carbonate-pitchblende type of mineralization; (b) sulfide type of mineralization; (c) arsenide type of mineralization (Ag-Bi-Ni-

[1] Regular preparation of reviews of this journal is supported by a grant from the National Science Foundation.

[2] An ore field is a group of deposits which are geologically similar and have a similar ore genesis.

Cu-U formation); (d) zones of fracturing and crumpling with dispersed and finely-dispersed uranium oxides; (e) uranite-magnetite type of mineralization; and (f) zones of strong albitization of shales and phyllites (with uraninite, zircon, and other minerals).

Uranium may migrate in ascending solutions saturated with hydrogen sulfide in the form of UCl_4, UF_4, or complex compounds. Above the reducing medium, where sulfides predominate, the presence of oxygen causes the precipitation of UO_2. The upper limit of distribution of uranium in veins depends on the depletion of uranium-bearing solutions. In zones of strong oxidation U^{4+} goes over to U^{6+}. Compounds of U^{6+} are removed if no silica is present in residual solutions. Precipitation may occur only if the solutions are permeating through coal beds, bituminous shales, and other rocks that reduce U^{6+} to U^{4+}. References are made mainly to uranium deposits in Czechoslovakia. Traditionally there are no direct characteristics of Russian uranium deposits.

V. S. Domarev and Yu. V. Bogdanov: Zoning of Mineralization in Cupriferous Sandstones of the Udokan Deposit (Pp. 25–34).

This is a preliminary report on the cupriferous sandstones of the Udokan Range in the Transbaikal region of Siberia, which were discovered in 1949. Mineralization of disseminated type is associated with fine- and coarse-grained sandstones and argillites of the Sakukan series of Proterozoic age. The distance between the extreme outcrops of this formation is 100 km. The ore-bearing horizon is characterized by cross-bedding and ripple marks.

There are six types of sedimentary ores characterized by the predominant mineralogical composition, such as pyrite, pyrite-chalcopyrite, chalcopyrite, bornite, bornite-chalcocite, and chalcocite. In some cases the amount of magnetite is 10 to 20 percent. The primary copper minerals are impregnated in the cement of sandstone—in places they form the entire mass of the cement—and accumulate in concretions and in veinlets. The last two are of diagenetic or metamorphic origin.

The zoning is illustrated by the development of bornite, taking the place of chalcocite farther away from the original shore line of the basin of deposition. The chalcopyrite zone develops still farther offshore, followed in turn by the pyrite zone.

The chalcocite-bearing, and to a certain extent the bornite-bearing sandstones, are generally of reddish color, while the chalcopyrite-pyrite-bearing sandstones, as a rule, are gray or greenish. In one case the thickness of the lower zone is 50 m, and that of the upper zone is 30 m. In a southeastern direction the zone of chalcocite goes over after 800 m into the zone of bornite. It is assumed that sedimentation in the Udokan developed under conditions of regression. There is reason to believe that a considerable change may be expected in deeper parts of the deposit due to change of facies.

The distribution of primary copper minerals may be complicated by metamorphism. Chalcopyrite may form from chalcocite and bornite. Quartz veins with some ore minerals cutting across the bornite and chalcocite ore zones are of Alpine type. The secondary zoning caused by alteration is of no importance in the Udokan. The zone of oxidation is negligible, as well as the zone of secondary enrichment. Parallels are drawn between deposits of the Udokan, Mangyshlak Peninsula, Northern Rhodesia, and some of the deposits of Dzhezhazgan in Kazakhstan.

V. I. Gryaznov and Yu. I. Selin: Basic Geological Features of Manganese Deposits of Bol'shoi Tokmak (Pp. 35–55).

The presence of manganese carbonate ore in cores from water wells in the town of Bol'shoi Tokmak was first discovered in 1939 at a depth of 110 m, some 40 km to the east of the famous manganese deposit at Nikopol. The deposit is located in the northeastern part of the Black Sea depression along the Ukrainian crystalline massif. The thickness of sedimentary rocks increases in the direction of the depression, and the near-shore facies of sediments grades into deeper facies. The stratigraphic sequence consists of Precambrian, Upper Cretaceous, Tertiary and Quaternary deposits. The manganese ore bed is associated with sands of the Kharkov stage of Oligocene age. There is a gradual transition from sandstones to manganese ore. The ore bed is located at a depth of from 60 to 140 m and dips at 2.5 to 6 m per km. The area occupied by the ore bed has the form of a crescent cut off in the west by the Dnieper River and directing its pointed end to the south. It is about 90 km long and some 25 km wide in its northern part. Shark teeth, Balanus, and shells of molluscs occur in the ore bed.

The deposit demonstrates a typical pattern of sedimentary marine manganese ore facies. In the northern part of the deposit the oxide ores gradually pass over in a southern direction into carbonate ores. In the transition zone the upper part of the ore bed consists of oxide ores (manganite), and the lower of carbonate ores. The manganite ore is represented by an earthy mass with psilomelane, lumpy porous ore that forms a continuous bed, and pisolitic ore with concretions up to 10 cm in diameter. The carbonate ores consist of a complex of carbonates, transitional between rhodochrosite and calcite. This type of ore forms a continuous bed or consists of concretions enclosed in clay.

The central part of the deposit is occupied mainly by the massive, continuous ore bed. Lumpy-concretionary ores form the eastern and the western zones of the deposit. Raw ore contains on the average 23.22% Mn. With the discovery of this deposit, the fact of continuous ore deposition along 200 km of Tertiary shore line (Nikopol and Bol'shoi Tokmak taken together) is established.

Oxide ore formed in shallow bays, with sufficient aeration and preservation of oxidation conditions during the diagenesis. Farther offshore the manganese compounds formed carbonates under reducing conditions of diagenesis.

G. I. Gorbunov: Principles of Distribution of Sulfide Copper-nickel Deposits in the Region of Pechenga (Kola Peninsula) (Pp. 56–69, two plates).

The copper-nickel ore field is located within the Pechenga series, which outcrops in the form of an arch. The series lies on Archean basement and consists of four covers of diabase, metadiabases, porphyrites, and tuffs, each 1,000 to 4,000 m thick. All these covers are separated by rocks of sedimentary origin. The copper-nickel mineralization is associated with tuffaceous-sedimentary formations located between the third and fourth covers and intruded by basic and ultrabasic rocks.

The formation of intrusions was simultaneous with folding. The first phase of intrusions is represented by barren gabbro-diabase. The second phase resulted in intrusion of nickel-bearing ultrabasic and basic rocks. There are 110 such intrusions, forming bedded bodies 200 to 7,000 m long and up to 600 m thick. The third phase of magmatic activity is characterized by a complex of dikes. The intrusions are differentiated and non-differentiated. The differentiated intrusions consist in their lower part of serpentinites, pyroxenites, gabbro, and monzonite

gabbro. The non-differentiated intrusions consist predominantly of serpentinites, or of gabbro. The lower parts of serpentinites in differentiated intrusives contain disseminated nickel and copper sulfides. Pyroxenites and gabbro contain pyrrhotite. There is a relation between the hydrothermal metamorphism of ultrabasic rocks and sulfide mineralization.

Copper-nickel deposits were formed during the conclusive period of tectonic movements. The movement of ore solutions and ore deposition occurred along intraformational tectonic zones, having a west-east strike. The process of mineralization was accompanied by tectonic movements and additional fracturing of rocks. The principal ore minerals in all types of ore are pyrrhotite, pentlandite, and chalcopyrite. Ilmenite, pyrite, marcasite, violarite, sphalerite, valleriite, bornite, and galena are minerals of secondary importance. Magnetite is one of the principal minerals in mineralized serpentinites.

All ore deposits of economic importance are concentrated in the central part of the ore field. Intersections of intraformational tectonic zones by the transversal reversed faults are very favorable for the deposition of massive ore. In almost all deposits contact of intraformational tectonic zones with the intrusives occurs in hinges of synclines. The mineralization fills voids in breccia of the tectonic zone, replaces the wall rock metasomatically, especially the serpentinites, and in places penetrates into phyllites. The non-differentiated intrusives, consisting entirely of serpentinites, are mineralized in cases where they are in contact with the tectonic zone. As a rule, thin serpentinite bodies are very prospective if located along the presumed trend of the tectonic zone.

Pyroxenites and metamorphosed pyroxenites are of secondary importance as ore-bearing rocks. Low-grade disseminated copper-nickel mineralization is associated with primary banding in intrusive bodies. The accumulation of sulfides is evidently the result of differentiation during the crystallization of intrusive bodies. Economic ore deposits, which have a structural control, were formed by solutions derived from the same magmatic source. The separation of sulfides occurred probably at greater depths in the magmatic chamber. The ore minerals crystallized under hydrothermal conditions. This is indicated by the wall rock alteration and by the presence in ore of serpentine, chlorite, and talc. At the end of the process of mineralization there was a change of physico-chemical conditions of ore deposition due to increase of the amount of hydrogen sulfide, carbon dioxide, and oxygen in residual solution. This is indicated by the appearance of pyrite, violarite, siderite, and magnetite (formed as the result of replacement of pyrrhotite and pentlandite) in upper parts of the deposits.

During prospecting and exploration it is necessary to take into account the possible change of ore facies along the strike and down the dip. The author summarized the results of geological study after the Second World War of the area of Pechenga (Petsamo) which was ceded to the Soviet Union by Finland. Photographs of ore samples represent ore breccia, massive ore and the network of veinlets in mineralized serpentinite and phyllite.

A. I. Pukharev: Geology and Peculiarities of Localization of the South-Yakutian Iron Ore Deposits (Pp. 70–76).

The principal metasomatic ore deposits of South Yakutia are enclosed in dolomites and marbles of the Fedorov sub-series of the Archean Iengra series. Along the strike and down the dip, the dolomites are partially or entirely replaced by the magnesial skarns and magnetite ores that are enclosed in skarns. Rocks of the

producing horizon are underlain and covered by schists. All metamorphic rocks are intensely migmatized and granitized. These processes were accompanied by intrusions of Archean alaskites and biotite-amphibole granites, forming concordant injections in migmatized metamorphic rocks. The magmatic processes alter the composition of the producing horizon and locate the areas of potential mineralization.

Complication of folded structures and flexures impaired locally the progress of mineralization. The iron-ore bodies are concordant deposits of bedded form within the dolomites, where they do not occupy any particular stratigraphic position. However, the lower horizons of dolomites are more prolific at the contacts with migmatites. Some ore bodies are associated with metasomatically altered gneissose beds, especially at the contacts with magnesial skarns. Ores formed by replacement of dolomites contain 55–58% Fe, and those replacing aluminum silicate rocks contain 35–42% Fe. The latter have a higher stratigraphic position than the ores emplaced in dolomites.

Boron mineralization is intimately associated with the iron ore bodies, and forms halos around the blind ore bodies. Tourmaline (boron) mineralization does not occur outside the iron deposits. Pyrrhotite, pyrite, chalcopyrite, and some molybdenite are present in the iron ores. Copper content due to chalcopyrite is up to 1 per cent. The latter mineral is genetically associated with magnetite of the Archean skarn formation and mineralization. Special attention is given to the possibilities of discovering blind iron-ore bodies.

I. Ya. Nekrasov: Genetic Types of Tin Deposits in Polousnyi Range and Selennyakh Ridge (Pp. 77–89).

The Polousnyi Range has a west-eastern trend, is 350 km long, and is located between the rivers Yana and Indigirka in northeastern Yakutia, in Siberia. In the west the Polousnyi Range joins with Tas-Khayakhtakh Range and acquires a meridional trend. The Deputat group of tin deposits is located at the site of the maximum bend of the range. Longitudinal and transversal, 80 to 100 km long, tectomagmatic zones are developed here. The stratigraphic sequence consists of 1,500 m of Precambrian metamorphic rocks, about 8,800 m of Paleozoic sediments, 7,000 m of Mesozoic, predominantly sedimentary deposits and some sedimentary-effusive rocks, and 300 to 350 m of Tertiary andesites and basalts.

All formations, with the exception of Tertiary rocks, are intruded and altered by intrusives ranging in age from Precambrian to Mesozoic. Two centers of mineralization are the above-mentioned Deputat area and the Omchikandin, in the central part of the range, within outcrops of Jurassic formations. The quartz-cassiterite mineralization is characterized by greisens forming stockworks 15 m thick, and 60 to 80 m long, and containing wolframite and topaz, and quartz-topaz-sulfide veins. It is associated with a group of Mesozoic intrusives in the Omchikandin area, which are concordant with the west-east strike of Mesozoic structure. The non-economic tin-bearing pegmatites emplaced in the apical parts of granite massifs contain tourmaline, monazite, and molybdenite. Primary fractures in granites control the formation of quartz-cassiterite deposits, which are older than the cassiterite-sulfide mineralization. The cassiterite-sulfide mineralization in the Deputat group of deposits is associated with younger granites intruded along fractures of submeridional strike, and forms skarns containing cassiterite, magnetite, with boron-bearing minerals, garnet, and pyroxenes.

Skarns were followed by the formation of hydrothermal ores containing pyrrho-

tite, arsenopyrite, molybdenite, cassiterite, stannite, chalcopyrite, sphalerite, and scheelite. Fractured zones due to shear are the structural factor controlling the deposition of cassiterite-sulfide ores. The consanguinity of tin mineralization with granites is established by the higher content of cassiterite and wolframite in granites. The tin-tungsten deposits are genetically related to granites of higher acidity and stronger alkalinity. The process of mineralization involved the transformation of true solutions into colloidal solutions and deposition of colloform and cryptocrystalline aggregates of cassiterite and quartz in the fractured zones.

V. A. Vakhrushev: Colloform Formation of Garnet and Molybdenite in Ores of the Shalym Deposit (Gornaya Shoriya) (Pp. 90–98, four plates).

Colloform aggregates of garnet and molybdenite occur in ferruginous skarns of the Shalym deposit in Western Siberia. Skarns are enclosed in syenites and albitized keratophyres with relics of sedimentary rocks.

Colloform garnet of andradite-grossular type is the main component of the skarns. Garnet has a concentric zonal structure, forms botryoidal aggregates up to 5 cm in diameter, and also lines the voids. Fissures, similar to desiccation fissures in gels, are characteristic of separate concentric rings. Fine-grained aggregates of carbonate and chlorite occur between the separate rings of garnet. Colloform garnet formed as the result of activity of the residual hydrothermal solutions after the formation of skarns. Crystalline garnet was dissolved and redeposited in the form of fine-grained and cryptocrystalline aggregate.

Molybdenite occurs in the Shalym deposit in the form of spherulites and botryoidal aggregates from 1 to 10 mm in diameter, formed in voids and fractures. These spherulites have a radial-acicular and concentric structure. The core of spherulites consists in places of minute cherty particles. Fibrous quartzine occurs in peripheral parts of some molybdenite spherulites. Quartzine also fills the fissures going toward the center of aggregates. The concentric layers of molybdenite are separated by fine quartz grains and liquid inclusions. These features indicate that the mineral was deposited from colloidal solutions. This study supports the opinion of A. G. Betekhtin, F. V. Chukhrov, and others about the major role of colloidal solutions in mineralization and deposition of minerals in the form of gels.

Photomicrographs demonstrate the mineral structure of colloform garnet and molybdenite.

Brief Communications

I. N. Pen'kov: Paragenetic Relations of Minerals in Hypogene Ores of the Chinasyl-Sai Deposit (Pp. 99–102).—The lead zinc deposit of Chinasyl-Sai is located in Southern Kazakhstan. It is characterized by the superimposition of several stages of mineralization, accompanied by oxidation-reduction reactions. The mineral associations correspond to the stages of mineralization, and are represented by (1) quartz-hematite; (2) ankerite, sphalerite, galena, and chalcopyrite; and (3) quartz-dolomite stages. Products of reactions are the iron-bearing minerals, pyrite, mushketovite, siderite, ankerite, ferrous chlorite, and bornite. Iron content in sphalerite depends on the concentration of iron in the mineralizing solution and on physico-chemical conditions of the medium. Black sphalerite forms under more reducing conditions than the light variety.

N. N. Mozgova: Replacement of Sulfides by Carbonates and Quartz of Later Generation in the "Verkhnii Rudnik" (Tetyukhe) Deposit (Pp. 103–106).—There

are two stages of mineralization in this Far Eastern deposit. The first is characterized by the association of hedenbergite and other skarn minerals with sulfides, and the second stage is represented by an association of later carbonates and quartz with other low-temperature minerals forming veinlets and replacing the minerals of the first stage. Arsenopyrite, sphalerite, pyrrhotite, galena, and chalcopyrite form a series of minerals arranged according to their increasing solubility, arsenopyrite being the least soluble and the least subject to replacement.

A. F. Korzhinskaya and E. K. Vasil'ev: Occurrence of Chillagite in Tungsten-bearing Veins of the Dzhidinskoe Deposit (Pp. 107–108).—Chillagite is the secondary mineral of a composition $Pb(W,Mo)O_4$ formed in the zone of oxidation in areas with a higher concentration of lead, tungsten, and molybdenum. Results of X-ray studies indicate that the mineral occupies an intermediate position in the isomorphic series of wulfenite-stolzite.

Professional Events

W. S. Zontov reports on the Second International Conference for the Peaceful Use of Atomic Energy, which took place in Geneva in September, 1958 (pp. 109–111).

T. N. Shadlun presents the results of the All-Union Conference on Evaluation of Scientific Principles of Prospecting for Blind Ore Bodies held in Moscow on November 18–24, 1958 (pp. 112–119). Five hundred geologists representing 60 institutions participated in this conference. The topics discussed dealt with the utilization of hypogene zoning in prospecting for blind ore deposits of hydrothermal origin, structural and lithological criteria in prospecting for blind ore bodies, geochemical prospecting for lead-zinc and rare metals deposits, prospecting for the deep-seated ore deposits through the study of primary halos of dispersed elements, geophysical methods of prospecting, the role of minor intrusives and dikes in localization of ore bodies, prospecting criteria for ore in skarns, hydrochemical prospecting, and specific case histories. This report is followed (pp. 120–125) by the resolution of the conference relative to structural geological studies, geophysical methods, geochemical and mineralogical, and petrological methods of prospecting.

D. G. Sapozhnikov gives an account of the Conference on Problems of Study of Regularities in Distribution of Mineral Deposits in Sedimentary Formations, held in Moscow on November 27–28, 1958 (pp. 125–127). The conference was concerned with the types of sedimentary ore formations, jaspilite formations of the volcanogenic cherty series of Karsakpai synclinorium, geological regularities in distribution of cupriferous sandstones in Central Kazakhstan and the Northern Tien-Shan mountains, continental formations of Cretaceous and Tertiary deposits of the southern part of the Urals-Siberian epi-Hercynian platform and the distribution of mineral deposits, and principles of formation and distribution of placers in different climatic regions.

I. I. Ginsburg reports briefly on the activities of the Commission of the Academy of Sciences of the Soviet Union on the Study of Clays (pp. 127–128).

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SHORT REVIEWS OF RECENT RUSSIAN BOOKS

Doklady Sovetskikh Geologov, Mezhdunarodnyi Geologicheskii Kongress, XXI Sessiya, 1960. [Contributions of the Soviet Geologists, International Geological Congress.] Gosgeoltekhizdat,Moscow, 1960. 20 vols. Price, 216r. 90k.

Only about a tenth of the Russian contributions to the International Geological Congress were printed in the official *Proceedings;* but every one of the 300-odd Soviet papers is published in full in this complementary series of volumes, in most cases with a long English summary. The twenty volumes correspond to twenty of the twenty-one sections of the Congress; and there are further publications relating to the International Association for Sedimentology (*27* papers, 11r. 20k.), the International Commission for the Study of Clays (15 papers, 7r.), and the International Association of Hydrogeologists (46 papers, 21r. 80k.). No contributions are made to the section on "The Genesis of Uranium and Thorium Ores." The price of the collection is rather high ($45–$50), more than the full cost of Congress membership; and the size of the edition, 2,500, suggests that despite the English summaries a widespread circulation outside the U.S.S.R is not contemplated. The publication is the first to quote prices both in light roubles (the present currency) and heavy roubles (the new currency after 1st January 1961, when one new rouble will equal 10 old ones).

Geologiya halogennykh otlozhenii SSSR. [Geology of the halogen deposits of the U.S.S.R.] By A. A. Ivanov and Yu F. Levitskii. Pp. 424, figs. 65, + 7 separate maps and sections. Gosgeoltekhizdat, Moscow, 1960. Price, 31r. 35k.

The title is somewhat of a misnomer, for the term halogen is used in a literal sense and the work deals solely with evaporite deposits. The stratigraphy and tectonogenesis of these formations within the Soviet Union are described in much detail, each chapter dealing with a separate geological system. Evaporites are present in every system from the (Lower) Cambrian onwards, except in the Trias. From the economic aspect the succession of importance, from greatest to least, is Permian, Neogene, Devonian, Cambrian, Jurassic, Cretaceous, Paleogene, Carboniferous, Ordovician and Silurian. Potash deposits are found in the first five. No pre-Cambrian evaporites are recognized.

Problemy geokhimii. [Problems of geochemistry.] No. 1. Pp. 300 (Russian), 301–316 (English summary). University Press, Lvov, 1959. Price 15r. 70k.

This new geochemical journal from the University of Lvov promises to maintain the same high standard as the mineralogical and geological magazines published there. The first number comprises 11 papers, the most important being one of 184 pages by E. N. Eliseev which deals with the geochemistry of the provinces of copper-nickel sulphides throughout the U.S.S.R.

Mineralogiya vyverzhenykh kompleksiv Zakhidnoi Volyni. [Mineralogy of the igneous complexes of Western Volhynia.] By E. K. Lazarenko and others. Pp. 509, figs. 262, University Press, Lvov, 1960. Price 29r. 35k. (Ukrainian, with English and Russian summaries.)

A well-produced monograph reviews the petrographic and petrogenetic studies conducted at the University of Lvov over the last 14 years, including investigations

on the Archaean (Zhitomir-Kirovograd) granitization, the Proterozoic granites, and the dolerites and effusive formations (principally basic rocks) of Riphean (= Beltian) age. Most of the work is concerned with the mineralogy of these rock complexes (with 85 mineral species), paying special attention to the hydrothermal and supergene alterations of the Riphean basalts. These contain native copper in masses weighing close on a kilogram, and rare minute specks of native iron. The English summary is six pages long.

Geologiya mestorozhdeniya redkykh elementov. [Geology of deposits of the rare elements.] No. 5, Minerals of germanium and their deposits. Pp. 112, price 5r. 45k. No. 6, Rare elements in bauxites. Pp. 48, price 2r. 10k. Gosgeoltekhizdat, Moscow, 1959. (Russian only.)

The booklets in this series are based entirely on published literature, which has been thoroughly combed. In each case there is a full bibliography of Western and Russian works.

Uranovye provintsii [Uranium provinces.] By M. M. KONSTANTINOV and E. YA. KULIKOVA. Pp. 306, figs. 170 + map. Atomizdat, Moscow, 1960. Price, 15r. 20k.

In yet another extensive review of the world's uranium deposits all the information has been assiduously compiled from Western literature (published mostly before mid-1957) and again there is nothing whatever about the Communist territories. Many small errors of fact have been introduced and the work is necessarily quite uncritical; but on the whole it presents a comprehensive though somewhat out-of-date appreciation of the resources of the Western powers.

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Geology for South African Students, 4th Edit. By G. N. G. HAMILTON and H. B. S. COOKE. Pp. 441; figs. 112. Central News Agency Ltd., Johannesburg, South Africa, 1960. Price, 30/.

The first edition appeared in 1939, and this 4th edition is considerably revised and enlarged. It is meant for an extremely elementary textbook for students in the Union of South Africa, S. W. Africa, and the two Rhodesias. The section on Physical Geology is brief, with the omission of theoretical considerations. It covers minerals, rocks, a few pages on general physical geology, structure, climate and landscape, paleontology, and historical geology. There are separate chapters on the stratigraphy of the southern Africa countries, and a chapter on economic geology. Appendices give the crystal systems, chemical symbols, blowpipe analyses, and tables of mineral determinations. Outside readings are listed for supplementary material. Included is a topographic map of southern Africa and a geological sketch map.

The book should prove satisfactory for the purpose for which it is intended, and others interested in southern Africa will find many helpful passages.

Physics of Precipitation, Geophysical Monograph No. 5. Edited by HELMUT WEICHMANN. Pp. 435. American Geophysical Union, Washington, D. C., 1960. Price, $12.50.

In June, 1959, the Second Woods Hole Conference on Cloud Physics was devoted to the *Physics of Precipitation,* and this volume contains the papers presented there, and the ensuing discussions. Some sixty authors participated in the presentation of fifty papers, which obviously cannot be considered in detail in a short review.

The subject matter of the technical papers is divided into five main groups, namely: The Morphology of Precipitation Clouds and Cloud Systems (6 papers); Morphology of Precipitation and Precipitation Particles (9); Fundamental Precipitation Processes (17); Hail Formation (9) and Artificial Precipitation Control (8 papers). The authors were drawn largely from American institutions, mostly active research and government institutions; American universities; and five distinguished foreign participants. The individual papers under the above five groups cover almost every field related to precipitation. Edited discussions follow each paper. Illustrations are plentiful, including one excellent color plate.

This comprehensive volume is a great contribution to the knowledge of precipitation, bringing together as it does authoritative information on the many and diverse phases of the problems of precipitation. It will serve as an outstanding reference to all students of meteorology and geology.

Crystal-Structure Analysis. By MARTIN J. BUERGER. Pp. 668. John Wiley & Sons, New York, 1960. Price, $18.50.

This book is a companion to the author's earlier volumes on *X-Ray Crystallography,* and *Vector Space and Its Application in Crystal Structure Investigation.* It developed from his notes prepared to direct post-graduate students. It formulates the methods and underlying theory for finding the location of atoms in crystal cells. The book reviews all of the available methods for analysis and indicates procedures for all the steps to be taken before proceeding with analysis. It provides a reader without previous background in the subject with the theory and methods to handle specific problems.

The book contains 23 chapters dealing with diffraction relations, quantitative aspects of diffraction x-rays by crystals, crystal-structure analysis. Following chapters deal with suitable materials, intensity measurements, and geometrical and physical factors. The author then takes up distribution of atoms in a cell; structure; projections; examples of determinations of simple structures; Fourier synthesis. This is followed by reciprocal space; symmetry in reciprocal space; applications to Fourier summations; phase determinations for heavy atoms and special cases. The last three chapters consider direct determinations; refinement; and calculations of interatomic distances and angles.

Like all Professor Buerger's books this volume is authoritative, complete, and clearly written. It should stand as the outstanding reference on the subject.

BOOKS RECEIVED

ROGER L. AMES AND JOHN E. COTTON

Science—The Endless Frontier. VANNEVAR BUSH. Pp. 220. National Science Foundation, Washington, D. C., (Reprinted 1960). *Reprinting of Dr. Bush's historic report to the President in 1945 on the need for an executive agency of the Federal Government, which led to the establishment of the National Science Foundation.*

Origin of Limestone Caves—A Symposium. GEORGE W. MOORE, Editor. Pp. 83. Bull. Nat. Speliological Soc., Vol. 22, Pt. 1, 1960. Price, $2.00. *Nine articles bearing on origin of caves; most caves were formed in a zone of saturation below a piezometric surface, aided by acids from chemical and biochemical processes.*

Geography in the 20th Century. Edited by GRIFFITH TAYLOR. Pp. 674; figs. 70. Philosophical Library, New York, 1960. Price, $4.75. *A reprinting of the 3rd enlarged edition of 1957.*

Summary Report to Coal Group, Geological Society of America, Concerning the Eleventh Meeting of the Nomenclature Commission of the International Committee on Coal Petrology. G. H. CADY and W. SPACKMAN. Pp. 36. *A short summary of the meeting, with an appendix that includes glossary pages approved by the Committee.*

Annual Report for the Year Ended 31st December 1959. MINISTER OF MINES, Province of British Columbia, pp. 302; figs. 32; tbls. 16. British Columbia Department of Mines, Victoria, 1960.

The British Solomon Islands Geological Record 1957–1958. JOHN C. GROVER, Editor. Pp. 113. Price, 35 s. Crown Agents for Oversea Governments and Administrations, London, 1960. *A series of 25 reports on investigations into the geology and mineral resources of the protectorate.*

The Australian Mineral Industry—Quarterly Review and Quarterly Statistics, Vol. 13, No. 1, September, 1960. Pp. 49. Price, 6/–. Australian Bureau of Mineral Resources, Geology and Geophysics, Canberra, 1960.

The Geology and Mineral Resources of the Dhali Area. I. G. GASS. Pp. 116; pls. 6; figs. 16; map, scale 1:31,680. Price, £1. Geological Survey of Cyprus, Memoir 4, Nicosia, 1960. *Surface indications of sulfide ore currently are being investigated. The Dhali area formerly supported a copper industry.*

XX International Geological Congress, Mexico, 1956. Section 5—Relations Between Tectonics and Sedimentation. Section 9—Geophysical Applications, Vols. 1 and 2; Commission on the Karroo System (Gondwana); Symposium on Geochemical Exploration, Vol. 1; Association of African Geological Surveys; Volume of Membership and General History of the Congress.

Water Inventory of the Maumee River Basin, Ohio. Pp. 112; pls. 46; figs. 6; tbls. 22. Price, $3.85. Ohio Water Plan Inventory Rept. 11. March, 1960. Ohio Department of Natural Resources, Columbus. *Expected increases in growth rate of the Maumee Valley water budget demand that new sources of supply be tapped.*

Bulletin of the Mineral Research and Exploration Institute of Turkey, Foreign Edition, No. 54, April, 1960. Ankara. *Six articles on tectonics, general geology, Permian algae, and garnet occurrences.*

Inventory of Washington Minerals. Pt. I, Second Edition, Nonmetallic Minerals. Vol. 1—Text, Vol. 2—Maps. G. M. VALENTINE; revised by MARSHALL T. HUNTTING, 1960. Pt. 1, pp. 175; pls. 39. Price per set, $3.00. State of Washington Geological Survey, Bull. 37, Olympia, 1960. *Resources are listed alphabetically with a brief description of each resource preceding the mention of its occurrence.*

University of California Publications in Geological Sciences—Berkeley and Los Angeles, 1960.

Vol. 36, No. 5. Stratigraphy and Paleontology of the Permian Nosoni and Dekkas Formations (Bollibokka Group). A. H. COOGAN. Pp. 73; pls. 6; figs. 23. Price, $1.75. *Stratigraphic and faunal descriptions are given for the Permian of northern California.*

Vol. 36, No. 6. A Survey of Various Late Cenozoic Vertebrate Faunas of the Panhandle of Texas. Part III. *Felidae*. D. E. SAVAGE. Pp. 26; figs. 6; tbls. 5. Price, 75 cents. *A study of the morphological description of the true cats of the Late Cenozoic.*

Vol. 38, No. 1. Volcanic History of the Guatemalan Highlands. HOWEL WILLIAMS. Pp. 86; pls. 13; figs. 8. Price, $2.00. *A petrographic history of the Tertiary and Quaternary vulcanism in Guatemala with detailed descriptions of the many Quaternary cones and domes.*

Geological Survey of Canada—Ottawa, 1960.

Catalogue of Type Invertebrate Fossils of the Geological Survey of Canada. Volume 1. THOMAS E. BOLTON. Pp. 215. Price, $2.50. *Includes fossil representatives of the Foraminifera, Porifera, Archaeocyatha, Stromatoporoidea, Anthozoa, Echinodermata, Graptolithina, Bryozoa, and Brachiopoda. Each type fossil is listed alphabetically by genus.*

Annual Report Calendar Year 1958. Pp. 143; maps, 2. Price, $1.00.

Memoir 300. Ground-Water Resources of the Brandon Map-Area, Manitoba. E. C. HALSTEAD. Pp. 67; figs. 6; tbls. 7; maps 2, scale 1:253,440. Price, 75 cents. *A brief outline of the bedrock and surficial geology provides background for discussion of the source, occurrence and movement of ground water and the recharge of aquifers.*

Bull. 66. Geological Interpretation of Aeroradiometric Data. A. F. GREGORY. Pp. 29; figs. 4; tbls. 2. Price, 50 cents. *The major variables in the measured intensity of gamma radiation are discussed and a technique for interpreting the regional geology is described.*

Paper 60-1. The Subsurface Gething and Bluesky Formations of Northeastern British Columbia. D. C. PUGH. Pp. 20; figs. 6; tbls. 2. Price, 50 cents. *Descriptions were made from drilling samples and well cores and the strata were correlated with the aid of electric logs.*

Paper 60-9. Shabogamo Lake, Newfoundland and Quebec 23G, E1/2. W. F. FAHRIG. Pp. 4. Map, scale 1:253,440. Price, 50 cents. *Metamorphism of iron-formation produced coarse-grained iron-oxide ores.*

Paper 60-13. Geology of Nictaux-Torbrook Map-Area, Annapolis and Kings Counties, Nova Scotia 21 A/14 (E 1/2), 21 A/15 (W 1/2). W. G. SMITHERINGALE. Pp. 32; tbls. 2. Map, scale 1:63,360. Price, 50 cents. *A few uneconomical manganese and iron deposits have been found in the region.*

Paper 60-14. Rice Lake-Port Hope and Trenton Map-Areas, Ontario 31 D/1, 30 M/16, 31 C/4, 30 N/13. B. A. LIBERTY. Pp. 4; 2 maps, scale 1"/1 mile. *A large part of the Oak Ridge Interlobate Moraine covers the area and greatly obscures the underlying structure.*

Universidad de Chile Instituto de Geologia—Santiago de Chile, 1960.

Publ. 13. Informe Sobre El Agua Subterranea En La Ciudad De Valdivia. JUAN KARZULOVIĆ KOKOT. Pp. 17. *An article on the effect of the May, 1960, earthquake on the groundwater supply for the city of Valdivia. In Spanish.*

Publ. 14. Los Movimientos Sismicos Del Mes De Mayo De 1960 En Chile. TAKEO WATANABE and JUAN KARZULOVIĆ KOKOT. Pp. 64; figs. 20. *A study of phenomena related to the earthquake shocks of May, 1960. The general geology is described; concludes that greatest damage occurred on recent sediment or where ground-water levels appear near the surface.*

Quarterly of the Colorado School of Mines—Golden, 1960.

Vol. 55, No. 2. Mineral Economics and the Problem of Equitable Taxation. O. H. LENTZ. Pp. 111. Price, $1.00. *A background study with chapters on the legislative rationale of percentage depletion; the analysis of the legislative rationale; percentage depletion and political economy; and problems of political economy and resource taxation in Colorado.*

Vol. 55, No. 4. On Fractures Caused by Explosions and Impacts. J. S. RINEHART. Pp. 155; figs. 75; tbls. 8. Price, $2.00. *The mathematics and physics of explosions with emphasis on the kinematics of induced stresses.*

Illinois Geological Survey—Urbana, 1960.

Bull. 88. Petroleum Industry in Illinois, 1959. Pt. 1. Oil and Gas Developments. Pt. II. Waterflood Operations. A. H. BELL, R. F. MAST, MARGARET O. OROS, C. W. SHERMAN, J. VAN DEN BERG. Pp. 127; pl. 1; figs. 5; tbls. 17. *Oil production in Illinois decreased by 5% from the 1958 production. Twelve oil and two gas pools were discovered during 1959.*

Circ. 303. Ceramic Tests of Illinois Clays and Shales. Compiled by W. ARTHUR WHITE and J. E. LAMAR. Pp. 72; fig. 1.

Circ. 304. Wisconsinan Molluscan Faunas of the Illinois Valley Region. A. B. LEONARD and J. C. FRYE. Pp. 32; figs. 3; pls. 4. *Molluscan faunas of the sediments representing the Altonian, Farmdalian, and Woodfordian substages are listed both geographically and stratigraphically.*

Circ. 305. Petroleum Coke in Illinois Coal Blends for Blast Furnace Coke. H. W. JACKMAN, R. L. EISSLER, and R. J. HELFINSTINE. Pp. 10; figs. 1; tbls. 6. *The best pilot-oven coke was produced from blends including 15 to 20 percent petroleum coke.*

Circ. 307. Chemical Evaluation of Illinois Oil Shales. W. J. ARMON and O. W. REES. Pp. 22; figs. 3; tbls. 11. *Four black shales and one limestone have assay yields ranging from 7.3 to 13.3 gallons of oil per ton of shale pyrolized.*

Circ. 308. Geochemistry of Carbonate Sediments and Sedimentary Carbonate Rocks. Pt. IV-A. Isotopic Composition Chemical Analysis. D. L. GRAF. Pp. 42; tbls. 4; 98 analyses. *A review of the literature on stable oxygen and carbon isotopes.*

Circ. 309. Geochemistry of Carbonate Sediments and Sedimentary Carbonate Rocks. Pt. IV-B. Bibliography. D. L. GRAF. Pp. 55. *Bibliography for previous four parts.*

Circ. 310. Coal in the Future Energy Market. H. E. RISSER. Pp. 15; tbls. 11.

Indiana Geological Survey—Bloomington, 1960.

Rept. of Progress 19. Engineering Geology of Dam Site and Spillway Areas for the Monroe Reservoir, Southern Indiana. J. D. WINSLOW, G. R. GATES and W. N. MELHORN. Pp. 19; pl. 1; figs. 2; tbls. 3. Price, 50 cents. *Summarizes the more significant geologic factors that will influence the design, construction and maintenance of the proposed Monroe Dam.*

Directory No. 8. Catalogue of Well Samples of the Indiana Geological Survey. T. A. DAWSON, D. M. SULLIVAN and A. J. HREHA. Pp. 458; figs. 4; tbls. 4. Price, $2.50.

Bull. 16. Geology and Coal Deposits of the Brazil Quadrangles, Indiana. H. C. HUTCHISON. Pp. 50; pls. 2; figs. 3; tbls. 2. Map, scale 1:24,000. Price, $2.50. *Approximately 400 million short tons of coal are present in the Brazil area in west-central Indiana.*

Bull. 17. Petrography of Indiana Sandstones Collected for High-Silica Evaluations. S. S. GREENBERG. Pp. 64; pl. 1; figs. 8; tbls. 9. Price, $1.00. *The Mansfield Formation of Lower Pennsylvanian age appears to be the best source of high-silica sand.*

U. S. Geological Survey—Washington, D. C., 1960.

Bull. 1072-J. Reconnaissance Geology of the Birney-Broadus Coal Field, Rosebud and Powder River Counties Montana. W. C. WARREN. Pp. 24; pls. 8; figs. 2; tbls. 3. *A description of 15 coal beds and reserves of coal in an area of 850 square miles in southeastern Montana.*

Bull. 1072-N. Stratigraphy of the Little Rocky Mountains and Encircling Foothills, Montana. M. M. KNECHTEL. Pp. 29; pls. 2; figs. 2; geologic map, scale 1:48,000. *Bedrock formations and surficial deposits mapped and described in relation to regional stratigraphy.*

Bull. 1072-P. Coal Resources of Arkansas, 1954. B. R. HALEY. Pp. 36; pls. 7; figs. 3; tbls. 10. *Recoverable reserves of 1,040 million short tons of bituminous coal are present in the Arkansas Valley coal field.*

Bull. 1087-F. Geology and Ore Deposits of the Kern River Uranium Area, California. E. M. MACKEVETT, JR. Pp. 53; pls. 7; figs. 4; tbls. 9. *Most of the small uranium deposits are distributed along fractures in the Isabella granodiorite. These deposits only contain local concentrations of ore.*

Bull. 1087-G. Uranium Content of Ground and Surface Waters in a Part of the Central Great Plains. E. R. LANDIS. Pp. 223–258; pls. 26; figs. 25; tbls. 4. Map, scale 1:10 mi. *The data are listed according to hydrologic source and they are believed to be of use in future hydrogeochemical exploration in the area.*

Bull. 1087-H. Geology of the Clay Hills Area, San Juan County, Utah. T. E. MULLENS. Pp. 77; pl. 1; figs. 2. Price, 75 cents. *Rocks exposed range in age from Permian to Jurassic and Quaternary. Unsuccessful uranium prospecting has been performed.*

Bull. 1093. Surficial Geology of Anchorage and Vicinity, Alaska. R. D. MILLER and ERNEST DOBROVOLNY. Pp. 128. Pls. 10; figs. 7; tbls. 7. Map, scale 1′: 63,360. *Surficial deposits in the Anchorage area are divisible into four main groups—pre-Wisconsin, Wisconsin, Pleistocene, and Recent. Five glaciations are recognized.*

Bull. 1096-A. Geology of the Grosvenor Quadrangle, Brown and Coleman Counties, Texas. R. T. TERRIERRE. Pp. 34; pls. 3; figs. 6; tbl. 1. *Pennsylvanian and Lower Permian stratigraphy between the Brazos and Colorado Rivers, north-central Texas has been mapped as stratigraphic equivalents to petroleum-bearing beds in West Texas.*

Bull. 1121-B. Illinoian Outwash in Southeastern Pennsylvania. W. N. LOCKWOOD and HAROLD MEISLER. Pp. 9; figs. 5; tbl. 1. *A highly weathered sand and gravel deposit overlain by unweathered outwash has been interpreted as Illinoian outwash.*

Bull. 1104-A. Erosion and Related Phenomena At Parícutin in 1957. KENNETH SEGERSTROM. Pp. 18; pl. 1; figs. 10. Price, 50 cents. *No appreciable compaction of ash occurred in the period 1947–57. Revegetation has greatly reduced the rate of erosion of ash.*

Bull. 1111-A. Devonian Rugose Corals from Northern Maine. W. A. OLIVER, JR. Pp. 22; pls. 5; figs. 2; tbls. 2. *Description of two new faunules from rocks of Helderberg and Schoharie age.*

Bull. 1112-B. Chemical Composition as a Guide to the Size of Sandstone-Type Uranium Deposits in the Morrison Formation on the Colorado Plateau. A. T. MIESCH, E. M. SHOEMAKER, W. L. NEWMAN, and W. I. FINCH. Pp. 17–60; figs. 3–14; tbls. 9. Price, 25 cents. *The concentrations of uranium, yttrium, sodium, iron, zirconium, manganese, calcium, and nickel in 75 mill pulp samples of uranium deposits of the Salt Wash member of the Morrison formation have been found to be related, statistically, to the size of the deposit represented by the sample.*

Bull. 1113. Second Report on a Cooperative Investigation of the Composition of Two Silicate Rocks. R. E. STEVENS AND OTHERS. Pp. 126; figs. 8; tbls. 21. Price, 40 cents. *A cooperative study to determine the accuracy and significance of quantitative analytical methods in geologic research.*

Bull. 1116-A. Geophysical Abstracts 180 January–March 1960. J. W. CLARKE. Pp. 128.

Bull. 1116-B. Geophysical Abstracts 181 April–June 1960. J. W. CLARKE. Pp. 129–279.

Bull. 1121-A. Classification of Wisconsin Glacial Deposits In Northeastern Ohio. G. W. WHITE. Pp. 12; fig. 1; tbl. 1. Price, 15 cents. *Four tills of Cary age are recognized.*

Prof. Paper 296. Geology of Glacier National Park and the Flathead Region, Northwestern Montana. C. P. Ross. Pp. 125; pls. 4; figs. 33. *A report on fieldwork and available data on the geologic, structural, and geomorphic studies of the rocks, ranging from Precambrian to Recent in age, in two adjacent mountainous regions of Montana.*

Prof. Paper 329. Reconnaissance of the Geomorphology and Glacial Geology of the San Joaquin Basin, Sierra Nevada, California. F. E. MATTHES. Pp. 62; pls. 2; figs. 48. Map, scale 1 inch: 1 mile. *An extension of Matthes' monumental work on the development of Yosemite Valley which has bearing on the geomorphic history of the Sierra Nevada Mountains as a whole.*

Prof. Paper 334-B. Fossils of the Littleton Formation (Lower Devonian) of New Hampshire. A. J. Boucot and Robert Arndt. Pp. 41–51; pls. 3; figs. 2; tbl. 1. Price, 25 cents. *Fossils from three localities in the Littleton formation in New Hampshire suggest a correlation of the strata with the Camden chert (Lower Devonian) of Tennessee.*

Prof. Paper 334-E. Upper Cretaceous Pelecypods of the Genus *Inoceramus* from Northern Alaska. D. L. Jones and George Gryc. Pp. 16; pls. 9; figs. 4; tbls. 2. Price, 45 cents. *A description of five species which are important guide fossils to the Upper Cretaceous rocks of the midwestern interior of North America and northern Alaska.*

Prof. Paper 334-F. Ammonites of Early Cretaceous Age (Valanginian and Hauterivian) from The Pacific Coast States. R. W. Imlay. Pp. 167–228; pls. 20; figs. 3; tbls. 4; chart 1. Price, $1.25.

Prof. Paper 334-G. Dispersion Characteristics of Montmorillonite, Kaolinite, and Illite Clays in Waters of Varying Quality, and Their Control with Phosphate Dispersants. B. N. Rolfe, R. F. Miller, and I. S. McQueen. Pp. 229–273; figs. 11; tbls. 20. Price, 40 cents. *A study is made of the dispersion characteristics of clay minerals in waters of different hardness and the relation of these characteristics to the control of canal seepage by artificial sedimentation.*

Prof. Paper 340. Trepostomatous Bryozoa of the Hamilton Group of New York State. R. S. Boardman. Pp. 87; pls. 22; figs. 27. Price, $1.25.

Prof. Paper 343. Geology and Ore Deposits of the Summitville District, San Juan Mountains, Colorado. T. A. Steven and James C. Ratté. Pp. 70; pls. 9; figs. 15; tbls. 7. Price, $2.00. Maps, scales 1:12,000 and 1:48,000. *The Summitville ores are of different age and genesis from the smaller mineralized districts several miles to the south.*

Prof. Paper 351. Mode of Flow of Saskatchewan Glacier, Alberta, Canada. M. F. Meier. Pp. 70; figs. 48; pls. 9; tbls. 11. *Contains the data of research on the measurement of velocity on the surface and at depth, the surface and bedrock topography, oblation and structures produced by flow.*

Prof. Paper 352-B. The Shape of Alluvial Channels in Relation to Sediment Type. S. A. Schumm. Pp. 17–30; pl. 1; figs. 9; tbl. 1. *If the silt and clay content in channels and banks of rivers increases downstream the depth of the river increases more rapidly and the width less rapidly with discharge than if the silt and clay content was constant.*

Prof. Paper 354-D. Early Cretaceous (Albian) Ammonites from the Chitina Valley and Talkeetna Mountains, Alaska. R. W. Imlay. Pp. 87–114; pls. 9; figs. 4; tbls. 3. Price, 50 cents. *The Early Cretaceous (Albian) Ammonites in southern Alaska have strong affinities with those in California and Oregon but are in part of Boreal and Eurasion origin.*

Prof. Paper 354-G. Deposition of Uranium in Salt-Pan Basins. K. G. Bell. Pp. 161–169; tbls. 3. Price, 20 cents. *Uranium may be adsorbed on clays that are deposited with some evaporite sediments. Where there are no organic-rich muds, clays, and phosphatic sediments deposited in evaporite sequences the uranium is deposited only upon final desiccation.*

Prof. Paper 355. Studies of the Mowry Shale (Cretaceous) and Contemporary Formations in the United States and Canada. J. B. Reeside, Jr. and W. A. Cobban. Pp. 126; pls. 58; figs. 30; tbls. 10. *A stratigraphic and paleontologic study of five large assemblages of gastroplitine cephalopods interpreted as five species of Neogastroplites having an unusual degree of variability.*

Water-Supply Paper 1302. Compilation of Records of Surface Waters of the United States Through September 1950. Pt. 1-B. North Atlantic Slope Basins, New York to York River. Pp. 679; pl. 1; figs. 2.

Water-Supply Paper 1304. Compilation of Records of Surface Waters of the United States through September 1950. Pt. 2-B. South Atlantic Slope and Eastern Gulf of Mexico Basins, Ogeechee River to Pearl River. Pp. 399; pl. 1; figs. 2.

Water-Supply Paper 1315-B. Compilation of Records of Surface Waters of the United States through September 1950. Pt. 11-A. Pacific Slope Basins in California except Central Valley. Pp. 413; pl. 1; figs. 3.

Water-Supply Paper 1420. Floods of August–October 1955 New England to North Carolina. D. B. BOGART. Pp. 854; pls. 6; figs. 51; tbls. 4. *This report contains descriptive material on the floods but its principal purpose is to present specific flood data.*

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SOCIETY OF ECONOMIC GEOLOGISTS[1]

PLANS FOR FEBRUARY–MARCH 1961 JOINT MEETING WITH AIME

The 1961 winter meeting of the Society of Economic Geologists will be held in St. Louis, Missouri, February 26–March 2, 1961, in conjunction with the American Institute of Mining, Metallurgical, and Petroleum Engineers. Headquarters for the meeting and all technical sessions and social functions will be at the *Chase-Park Plaza Hotel.*

The Society luncheon is scheduled for *12:15 p.m., on Thursday, March 2,* in the *Tiara Room,* top floor, Park Plaza Hotel. Bar facilities will be available prior to the luncheon for the use of any who may wish to purchase drinks. Luncheon tickets are $4.50 each. As usual, the tickets may be purchased from the AIME in advance, or at the Convention Registration Desk.

PROGRAM

A special symposium of more than usual interest to mining operators and management people will be held at this session. The subject is *Mining Geology-Methods, Techniques, and Results.* Several prominent mining geologists have accepted invitations to present papers which have been selected to cover a wide range in types of mineral deposits and operations, and should be of wide general interest to the mining industry.

WEDNESDAY, MARCH 1, 9:00–12:00 A.M., KHORASSAN C ROOM

Chairmen: DR. M. L. JENSEN AND J. D. FORRESTER

Some Aspects of Mine Geology in the Southeast Missouri Lead District: F. G. Snyder and James W. Odell—Mining geology in the Southeast Missouri district is regarded as distinct from exploration geology. The mine geologist has three objectives: (1) to assist profitable mine operation; (2) to extend the life of the mine by finding additional ore; (3) to interpret geology to operating staff and management. On the basis of his interpretation drilling programs are planned, orebodies are evaluated for development, and day-to-day problems are solved.

Under a mining geology program initiated in 1947, extensive underground workings have been mapped on a scale of 50 ft to 1 in., and a district pattern of ore controls has been established. The effectiveness of this program is revealed by production data and cost figures for the district.

The Use of Geology in Butte, Montana: Edward P. Shea—Since 1900, when it was organized, Anaconda's geological department at Butte has successfully employed standardized methods. Guided by the geologic record, the geologist works closely with mine operators, pursuing a policy of developing at least one ton of new ore to replace every ton mined. A formal estimate of reserves is made on the first of each year, and the geologist estimates the tonnage developed weekly to determine the current status. A geological research department with a well equipped laboratory is maintained to investigate rock alteration, and extensive

studies are in progress to relate alteration to mineralization and grade in both vertical and horizontal dimensions. An exhaustive study of Butte mineralogy is under way to obtain better knowledge and understanding of the behavior of the ore minerals at the time of deposition. This information will be used to predict deep-level possibilities and locate the zones of better copper mineralization. The value of former records is demonstrated by comparatively recent projects—such as the Kelley and Elm Orlu cave mines and the Alice and Berkeley pits—which originated in the geological department.

Role of Mine Geology in Exploitation of the Iron Deposits of the Knob Lake Range, Canada: Roger A. Blais and John B. Stubbins—Operations of the Iron Ore Co. of Canada in Labrador-New Quebec have, from the start, included a large amount of geological work. During the exploration phase, from 1936 to 1950, geologists directed the mapping of more than 15,000 sq miles of desolate and remote territory. They also supervised test pitting, drilling, under-ground workings, volume factor and structure tests, as well as calculations of ore grades and tonnages.

In the development phase, the orebodies are outlined in detail by mapping at 100 ft to the in.; systematic test pitting and trenching with power shovels; and test and tonnage drilling. Development is carried sufficiently ahead of mining to provide reliable tonnage and grade estimates and allow final mine planning. This work costs less than 5¢ per ton of ore outlined. All mines are mapped and plotted on plans and sections at 40 ft to the in. Geological interpretation and ore grades are revised daily on the basis of the mining data. To make full use of geology in the mining operations, the pit engineer combines the duties of geologist and mining engineer. Detailed mine geology in this district is a well recognized and relatively inexpensive necessity.

Geology at the Pitch Mine: Arthur Baker III and Wm. C. Scott—This 60-tpd high-grade uranium mine near Gunnison, Colo., offers an excellent small-scale example of the use of geology in an operating mine. Small limestone lenses, rarely containing more than 10,000 tons of ore, occur in a shear zone 300 ft wide. Both ore and surrounding rock are strongly sheared, making very bad ground that is costly to drive through and equally costly to hold open. Because of the small size of orebodies, much exploration work is necessary. Percussion long-holing is used for exploration; it has serious drawbacks but is the most effective and least expensive technique that has been found. So far the mine geologist has not been able to predict ore very far ahead of actual physical exploration; his task is careful study of all openings for the very subtle indications that there is ore nearby. On the basis of this work new orebodies have been found and known bodies have been mined as efficiently and cleanly as possible. It is probably no exaggeration to say that without the mine geologist's work the life of the mine would be halved.

Operations Geology for Kennecott Copper Corp.: Allan H. James—Within the large and complex Kennecott geological organization Operations Geology describes the activities of a small group of men resident at Kennecott's mines whose objectives are: (1) Determination of geological framework of Kennecott's porphyry copper mines. (2) Appraisal of district metalization. (3) Application of geology to engineering and production problems and distribution of information to other geological groups engaged in exploration, coordination and research. (4) Consultation and service in geological phases of operational and management problems.

These objectives are implemented by (1) Detailed district and pit mapping designed principally to develop men and their ideas and only secondarily for the production of high grade geological maps. (2) Development of drilling programs

and other proposals (based on men, ideas and information developed in 1) designed to appraise or inventory metal distribution in each mining district, regardless of its present economic or "ore" potential. (3) The specialization of individual geologists developed in 1 and 2, in geologic phases of mine economics-ore reserves, pit design and rock mechanics, hydrology, business, tax and legal problems. (4) The development of management confidence leading to calls for consultation and service in geological phases of the operation.

At our mines the details of the four phases of Operations Geology differ from that at many other mines, largely due to size and complexity of the organization, the great time lead necessary in large scale porphyry mine development and planning (with resultant need for flexibility and imagination in appraisals,) and the great economies which appear to be achievable with proper application of geology to appropriate parts of pit design, slope control and operation control.

Operations Geology is a staff service. The responsibility for execution of reserve estimation, pit design and operation control is in other segments of the organization. Results are effected by proposal and consultation.

A few geological problems are described.

Use of Punch Card Accounting Machines in Calculating Reserves at Sullivan Mine: A. C. Freeze—An electrical data processing system using punch cards has been developed by the Geological and Accounting Departments at the Sullivan Mine of The Consolidated Mining and Smelting Company of Canada Limited, Kimberley, B. C., as an important aid in calculating ore reserves more rapidly, accurately and with important savings especially in labor. The use of this equipment permits the storing and processing of a large volume of related information which through the years has proven to be of great value in formulating and reviewing current and long-range mining programs.

The paper outlines the mining situation for which the procedures were developed. It describes briefly the equipment used and the essential steps followed in computing reserves, beginning with the machine processing of drill core assays etc., and ending with the collation of all pertinent information concerning each ore block on a single punch card. It is then a simple matter to effect the final summations.

The routine calculation of specific gravity on one of the machines is based upon the relationship of specific gravity to the lead, zinc and iron content of the ore. It is believed to be unique and may be of interest to those working on ore bodies having large variations in the content of combined sulfides.

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SCIENTIFIC NOTES AND NEWS

DONALD H. YARDLEY, Professor on the Mineral Engineering staff of the University of Minnesota has been given a National Science Foundation grant for the sum of $25,500 to make a Study of Trace Element Distribution in a Swamp Environment. The objective of this work is to determine the nature of the geochemical distribution patterns of certain trace elements in a swamp environment overlying a mineralized contact. Another aspect is to investigate the factors which affect or control geochemical mobility and distribution in such an environment, and the relationship to neighboring environments overlying a similar geologic setting.

J. F. KAPNEK of Capetown and Philadelphia, who has instigated many explorations for mineral deposits in southern Africa, was made a Companion of the Order of the British Empire in the New Year Honours List in recognition of his services to the recently established University College of Rhodesia and Nyasaland in Salisbury, S. Rhodesia. Mr. Kapnek made the first contribution towards founding the College on D-Day, 1944, to commemorate the landing of British and American forces in Europe.

A new department of Geology is being established at the University College of Rhodesia and Nyasaland. Prof. G. Bond has put in a request for spare copies or duplicates of authors' reprints to be mailed to him. Those published in journals of limited circulation would be particularly welcome.

ROBERT W. DECKER, Professor of Geology at Dartmouth College and Distinguished Lecturer of the American Association of Petroleum Geologists, has recently returned from 18 months in Indonesia, where he taught geology at the University of Indonesia, Bandung. During the period he visited Anak Krakatau during two eruptions. Intermittent activity since 1927 has built a new island nearly one mile across and 500 feet high, replacing the original island, which sank into the sea during the 1883 eruptions.

DONALD H. MCLAUGHLIN has been named for the American Institute of Mining, Metallurgical, and Petroleum Engineers' Rand Medal for outstanding mining administration and contributions to education. Presentation will take place at the Annual Meeting in St. Louis in February.

ALEKSIS VOLBORTH, mineralogist with the Nevada Mining Analytical Laboratory, Mackay School of Mines, University of Nevada, has been invited to Washington, D. C., by the Smithsonian Institution to prepare and arrange a rare collection of pegmatite minerals and rocks from Finland. The Finnish collection will add some 2,000 carefully selected specimens, including rare beryllium and lithium minerals, to the Smithsonian's valuable mineral display, considered among the finest in the world.

PETER T. FLAWN has been named Director of the Bureau of Economic Geology and Professor of Geology at the University of Texas. He succeeds the late John T. Lonsdale as State Geologist for Texas.

An experimental deep-sea drilling program will be started in March near Guadalupe Island, off the west coast of Mexico, in 12,000 feet of water to test equipment and techniques for possible use in "Project Mohole," which it is hoped will determine the composition and properties of the crust and mantle.

Boston University has purchased for $9,000 the Wall Mineral Collection which contains more than 4,500 specimens, obtained from the widow of Milford W. Wall of Brookline. Some of the specimens can no longer be duplicated.

The A.A.P.G., S.E.P.M., and R.M.S. will hold annual meetings in Denver, Colo., April 24–27, 1961, with headquarters at the Denver Hilton Hotel. The theme of the meetings is "The Backbone of the Americas."

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FIFTIETH ANNIVERSARY VOLUME

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1905–1955

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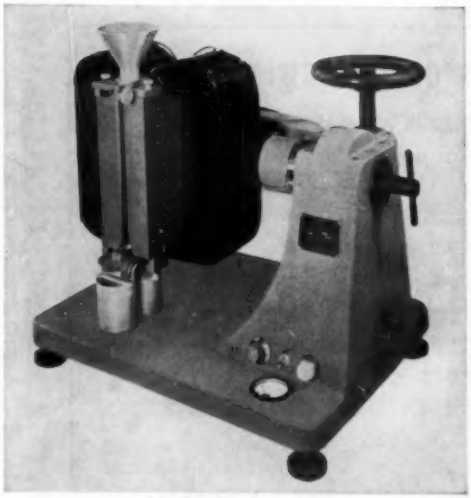

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